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Supporting Information

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Asymmetric Hydroxylative Phenol Dearomatization Via In Situ Generation of Iodanes from Chiral Iodoarenes and *m*-CPBA

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Supporting Information

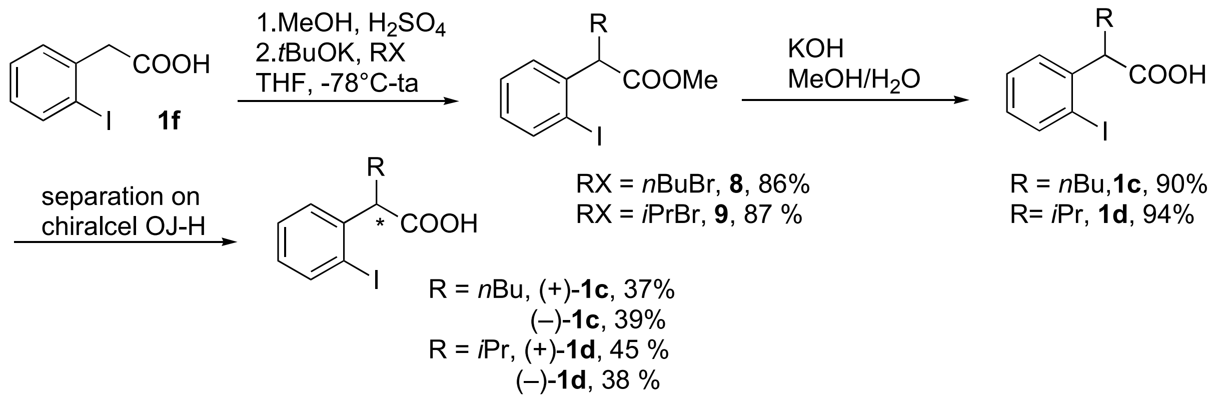
CONTENTS

General: All reactions were run under N_2. Dichloromethane (CH_2Cl_2) was purified by passage through alumina. Acetone and chloroform ($CHCl_3$) were purified by distillation. HPLC quality solvents were used for analytical and preparative HPLC work. Standard column chromatography was carried out under positive pressure using 40-63 µm silica gel and the indicated solvents. All commercial starting materials and reagents were used as received, except *meta*-chloroperbenzoic acid (*m*-CPBA, 70% with *meta*-chlorobenzoic acid), which was partially dried overnight under high vacuum, and 2-methylnaphthol, which was purified by column chromatography, eluting with petroleum ether/ethyl acetate (EtOAc) (5:1).

Evaporations were conducted under reduced pressure at temperatures less than 45°C. Further drying of residues was accomplished under high vacuum, except for volatile compounds. Melting points are uncorrected. NMR spectra of samples in the indicated solvent were run at 250, 300 or 400 MHz. Electron impact mass spectra were obtained at 70 eV. Low and high resolution electron impact and chemical ionisation (EIMS, CIMS, ESIMS, HRMS) were obtained from the mass spectroscopy laboratory at the Institut Européen de Chimie et Biologie, Pessac, France. Elementary analyses were obtained from the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Rennes, France. Preparative HPLC separations were performed using a Chiralcel OJ-H column (250 × 20 mm) on a Varian system equipped with ProStar 215 pumps and a ProStar 320 UV-visible detector. Analytical HPLC were performed using Chiralcel OJ-H and AS-H columns (250 × 4.6 mm) on a Thermo system equipped with P1500 pumps and a UV 6000LP diode array detector).

Preparation of Chiral Iodoarenes

Preparation of 1c and 1d



Methyl 2-(2-iodophenyl)hexanoate (8). To a stirred solution of 2-iodophenylacetic acid (**1f**, 3.250 g, 12.4 mmol) in MeOH (80 mL) was added conc. H_2SO_4 (8 mL). This solution was stirred during 3 h under reflux, then MeOH was evaporated and CH_2Cl_2 (100 mL) was added. The resulting solution was washed with a saturated aqueous solution of $NaHCO_3$ (4 × 50 mL) and brine (50 mL), dried over $MgSO_4$ and evaporated to give a crude product as a colorless oil. To this crude product was added a solution of *t*-BuOK (1.530 g, 13.63 mmol, 1.1 equiv) in dry THF (140 mL) at -78°C under N_2 and *n*-BuBr (1.605 mL, 14.9 mmol, 1.2 equiv) was added after 2 min. The reaction was allowed to warm up to rt and stirring was continued until complete conversion of the starting material was observed by TLC (ca.12 h). Water (50 mL) was added and the reaction mixture was extracted with Et_2O (3 × 50 mL). The organic layer was washed with an aqueous saturated solution of NH_4Cl (50 mL) and brine (50 mL), dried

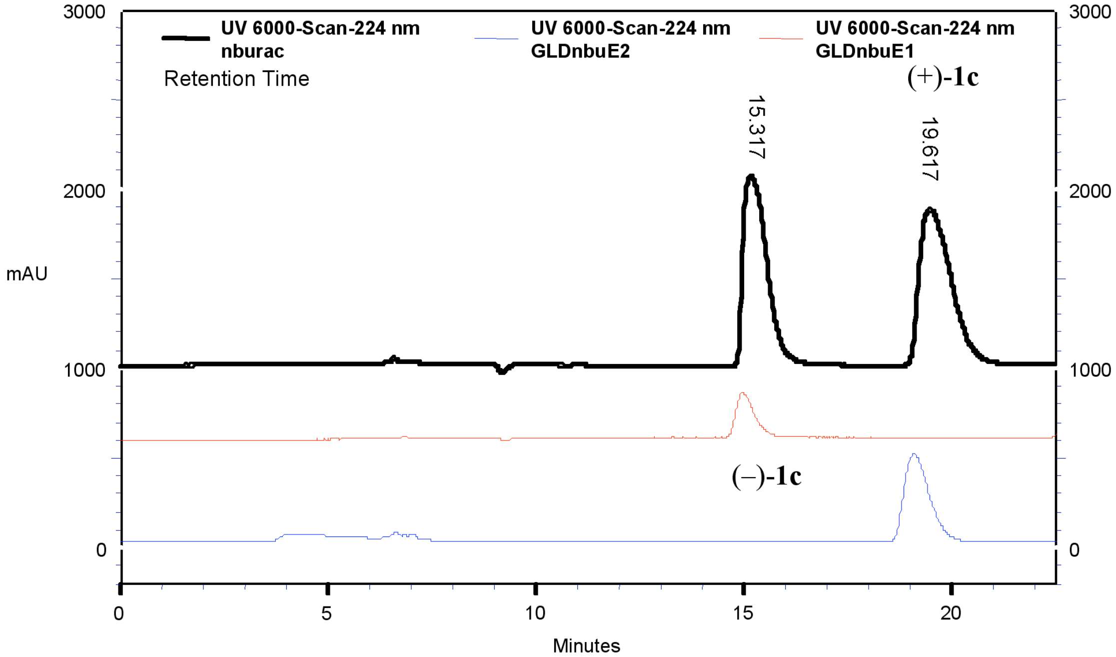
over $MgSO_4$ and evaporated to give a crude product, which was purified by silica gel chromatography (cyclohexane/EtOAc, 15:1) to furnish **8** (3.50 g, 86%) as a colourless oil. IR (neat) ν_{max} 2981, 1741, 1175 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.84 (dd, J = 0.9, 7.9 Hz, 1H), 7.27-7.37 (m, 2H), 6.93 (ddd, J = 2.1, 6.8, 8.9 Hz , 1H), 4.04 (t, J = 7.5 Hz, 1H), 3.66 (s, 3H), 2.08-1.96 (m, 1H), 1.80-1.67 (m, 1H), 1.43-1.17 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.0 (COO), 142.2 (Cq_{aro}), 139.7 (CH_{aro}), 128.7 (CH_{aro}), 128.6 (CH_{aro}), 127.7 (CH_{aro}), 101.6 (C-I), 54.8 (OCH_3), 51.9 (CH_{benz}), 33.4 (CH_2), 29.5 (CH_2), 22.5 (CH_2), 13.8 (CH_3); EIMS m/z (rel. intensity) 332 (M^+, 32), 273 (100), 205 (69), 146 (17), 89 (100); HRMS (ESI) calcd for $C_{12}H_{16}O_2I$ ($[M+H]^+$) 333.0352, found 333.0348.

Methyl 2-(2-iodophenyl)-3-methylbutanoate (9). To a stirred solution of 2-iodophenylacetic acid (**1f**, 5.24 g, 20 mmol) in MeOH (135 mL) was added conc. H_2SO_4 (13.5 mL). This solution was stirred during 3 h under reflux, then MeOH was evaporated and CH_2Cl_2 (250 mL) was added. The resulting solution was washed with a saturated aqueous solution of $NaHCO_3$ (4 × 75 mL) and brine (50 mL), dried over $MgSO_4$ and evaporated to give a crude product as a colorless oil. To this crude product was added a solution of *t*-BuOK (2.47 g, 22 mmol, 1.1 equiv) in dry THF (200 mL) at -78°C under N_2 and *i*-PrBr (2.25 mL, 24 mmol, 1.2 equiv) was added after 2 min. The reaction was allowed to warm up to rt and stirring was continued until complete conversion of the starting material was observed by TLC (ca. 16h). Water (75 mL) was added and the reaction mixture was extracted with Et_2O (3 × 75 mL). The organic layer was washed with an aqueous saturated solution of NH_4Cl (75 mL) and brine (75 mL), dried over $MgSO_4$ and evaporated to give a residue, which was purified by column chromatography (cyclohexane/EtOAc, 15:1) to furnish **9** (5.53 g, 87%) as a colourless oil. IR (neat) ν_{max} 2972, 1729, 1162 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.84 (dd, J = 1.1, 7.9 Hz, 1H), 7.49 (dd, J = 1.7, 7.9 Hz, 1H), 7.31 (td, J = 1.1, 7.9 Hz, 1H), 6.93 (td, J = 1.7, 7.9 Hz, 1H), 3.81 (d, J = 10.4 Hz, 1H), 3.66 (s, 3H), 2.41-2.28 (m, 1H), 1.08 (d, J = 6.4 Hz, 3H), 0.75 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.9 (COO), 141.3 (CH_{aro}), 139.6 (CH_{aro}), 128.8 (CH_{aro}), 128.6 (CH_{aro}), 128.2 (CH_{aro}), 102.7 (C-I), 61.9 (OCH_3), 51.8 (CH_{benz}), 33.0 (CH), 21.2 (CH_3), 19.5 (CH_3); EIMS m/z (rel intensity) 318 (M^+, 21), 275 (42), 259 (13), 191 (100); HRMS (ESI) calcd for $C_{12}H_{16}O_2I$ ($[M+H]^+$) 319.0195, found 319.0182.

2-(2-Iodophenyl)hexanoic acid (1c). To a solution of **8** (3.50 g, 10.6 mmol) in $MeOH/H_2O$ (3:1, 180 mL) was added KOH (1.784 g, 33.2 mmol). The resulting mixture was stirred at rt and after 5 h, 10 h and 15 h, additional amounts of KOH (2.56 g, 47.7 mmol) were added each

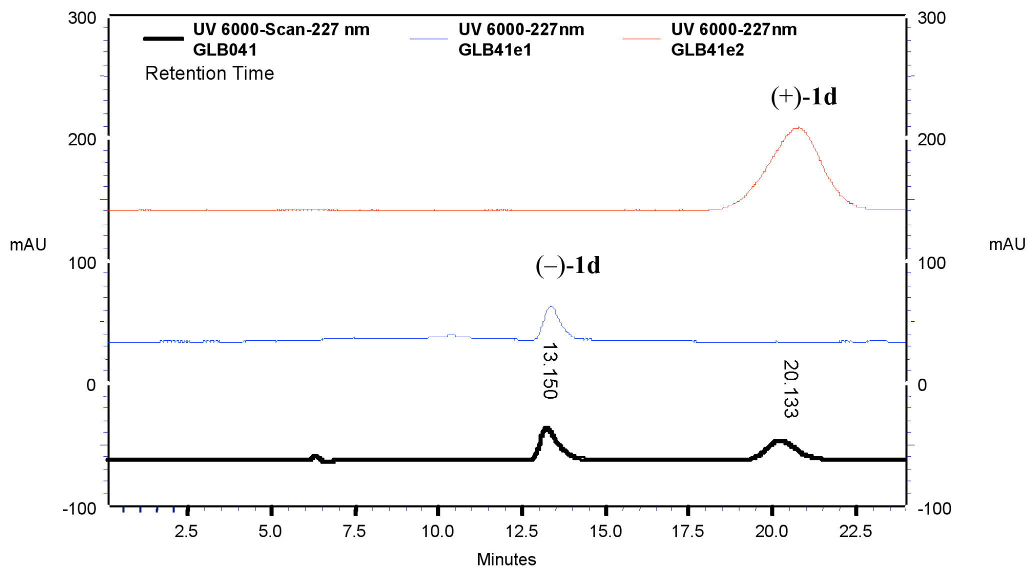
time. After 20 h, MeOH was evaporated and the aqueous layer was extracted with Et_2O (30 mL), then acidified to pH 1 with aq. HCl (10%), saturated with NaCl and extracted with EtOAc (4 × 50 mL). The combined organic layers were dried over $MgSO_4$ and evaporated to give a residue, which was purified by column chromatography (cyclohexane/EtOAc/AcOH, 6:1:0.1) to furnish **1c** (3.01 g, 90%) as a colorless oil. IR (neat) ν_{max} 3032, 2889, 2714, 2583, 1751, 1501, 1422, 1384, 1127 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.90 (brs, 1H, COOH), 7.86 (dd, J = 0.9, 7.9 Hz, 1H), 7.39-7.29 (m, 2H), 6.95 (ddd, J = 2.1, 6.8, 10.2 Hz, 1H), 4.09 (t, J = 7.5 Hz, 1H), 2.11-1.98 (m, 1H), 1.83-1.71 (m, 1H), 1.39-1.20 (m, 5H), 0.88 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.0 (COO), 141.6 (Cq_{aro}), 139.8 (CH_{aro}), 129.0 (CH_{aro}), 128.6 (CH_{aro}), 127.9 (CH_{aro}), 101.9 (C-I), 54.7 (CH_{benz}), 33.0 (CH_2), 29.4 (CH_2), 22.5 (CH_2), 13.8 (CH_3); EIMS m/z (rel. intensity): 318 (M^+, 21), 259 (24), 191 (100), 171 (6), 135 (31); HRMS (ESI) calcd for $C_{12}H_{14}O_2Na_2I$ ($[M+2Na-H]^+$) 362.9834, found 362.9820; HPLC analysis (column Chiralcel OJ-H, *n*-hexane/*iso*-propanol, 97:3, 0.5 mL/min, λ_{max} = 224 nm): Rt = 15.3 min and 19.6 min.

Separation of the two enantiomers was performed on a semi-preparative OJ-H column (*n*-hexane/*iso*-propanol, 99:1, 10 mL/min). 1.0 g of racemic 2-(2-iodophenyl)hexanoic acid afforded pure (–)-**1c** (369 mg, 37 %) and (+)-**1c** (393 mg, 39%). (–)-**1c**: $[\alpha]_D^{20}$ –76.9° (c 0.8, $CHCl_3$), Rt = 15.3 min; (+)-**1c**: $[\alpha]_D^{20}$ 80.1° (c 1.0, $CHCl_3$), Rt = 19.6 min.

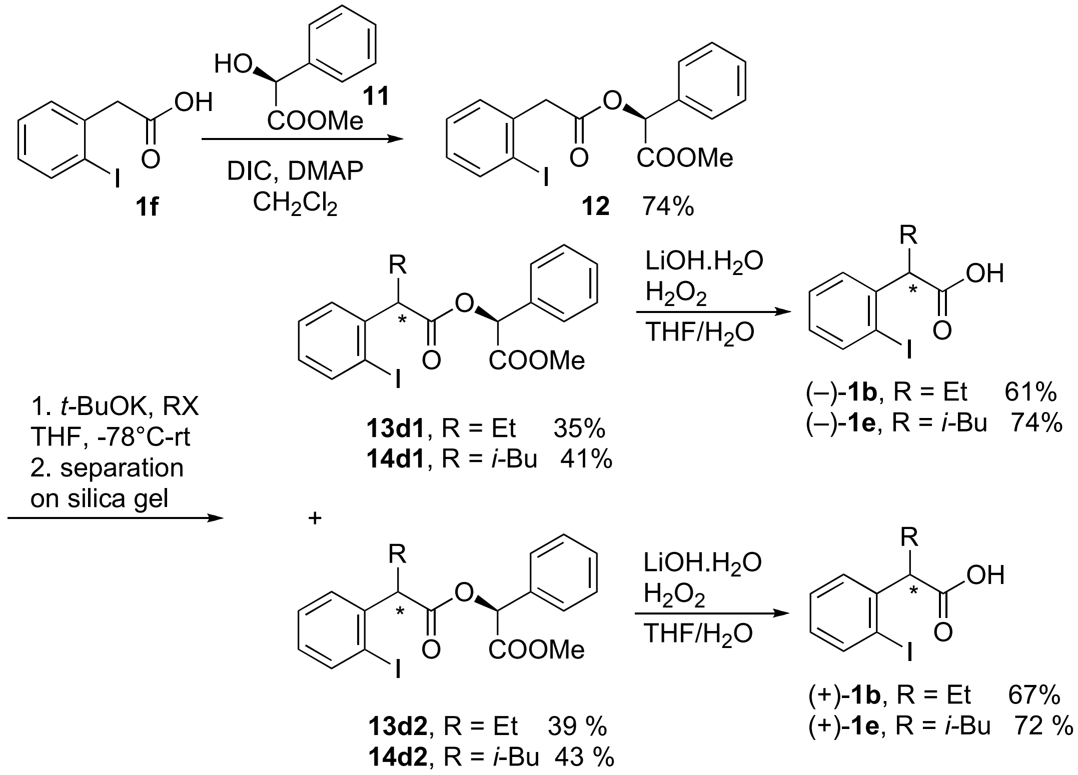


2-(2-Iodophenyl)-3-methylbutanoic acid (1d). To a solution of **9** (4.00 g, 12.66 mmol) in MeOH/H_2O (3:1, 200 mL) was added KOH (2.13 g, 38 mmol). The resulting mixture was stirred at rt and, each 10 h, additional amounts of KOH (2.13 g, 38 mmol) were added each time. After 120 h, MeOH was evaporated and the remaining aqueous layer was extracted with Et_2O (50 mL), acidified to pH 1 with aq. HCl (10%), saturated with NaCl and extracted with EtOAc (4 × 60 mL). The combined organic layers were dried over $MgSO_4$ and evaporated to give a residue, which was purified by column chromatography (cyclohexane/EtOAc/AcOH, 6:1:0.1) to furnish **1d** (3.61 g, 94 %) as a white solid. mp = 64°C; IR (neat) ν_{max} 3019, 2921, 2789, 2610, 1751, 1502, 1381, 1261 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.04 (brs, 1H, COOH), 7.85 (d, J = 7.9 Hz, 1H), 7.46 (d, J = 7.9 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 6.94 (td, J = 1.3, 8.2 Hz, 1H), 3.82 (d, J = 10.4 Hz, 1H), 2.39-2.26 (m, 1H), 1.11 (d, J = 6.2 Hz, 3H), 0.74 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.2 (COO), 140.8 (Cq_{aro}), 139.7 (CH_{aro}), 129.0 (CH_{aro}), 128.6 (CH_{aro}), 128.3 (CH_{aro}), 102.9 (C-I), 62.1 (CH_{benz}), 32.6 (CH_3), 19.5 (CH_3); EIMS m/z (rel. intensity) 304 (M^+, 41), 262 (44), 260 (12), 259 (49), 244 (47), 217 (53), 177 (77), 135 (100); HRMS (ESI) calcd for $C_{11}H_{12}INa_2O_2$ ($[M+2Na-H]^+$) 348.9677, found 348.9665; HPLC analysis (column Chiralcel OJ-H, *n*-hexane/*iso*-propanol, 95:5, 0.5 mL/min, λ_{max} = 227 nm) Rt = 13.1 and 20.1 min.

Separation of the two enantiomers was performed on a semi-preparative OJ-H column (*n*-hexane/*iso*-propanol, 95:5, 14 mL/min). 2.5 g of racemic **1d** afforded (–)-**1d** (1.125 g, 45%) and (+)-**1d** (950 mg, 38 %). (–)-**1d**: $[\alpha]_D^{20}$ –56.7° (*c* 1.3, $CHCl_3$), Rt = 13.1 min; (+)-**1d**: $[\alpha]_D^{20}$ 58.2°(*c* 1.1, $CHCl_3$), Rt = 20.1 min.



Preparation of 1b and 1e



Methyl 2-hydroxy-2-phenylacetate (11).[1] To a stirred solution of (*L*)-mandelic acid (**10**, 4.56 g, 30 mmol) in MeOH (100 mL) was added *p*-TsOH.H_2O (571 mg, 3 mmol, 0.1 equiv). The mixture was stirred at reflux for 3 h, after which time it was evaporated to give an oil. This oil was dissolved into CH_2Cl_2 (150 mL), washed with aq. sat. $NaHCO_3$ (3 × 100 mL) and brine (100 mL), dried over $MgSO_4$ and evaporated to furnish (+)-**11** (4.850 g, 97 %) as a white solid. mp= 57°C (lit.[1] mp = 55-56°C); IR (neat) ν_{max} 3528, 3441, 3032, 2978, 2827, 1738 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.44-7.32 (m, 5H), 5.18 (d, J = 5.3 Hz, 1H), 3.76 (s, 3H), 3.44 (d, J = 5.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.1 (COO), 138.2 (Cq_{aro}), 128.6 (CH_{aro} × 2), 128.5 (CH_{aro}), 126.6 (CH_{aro} × 2), 72.9 (CH_{benz}), 53.0 (OCH_3); EIMS *m*/*z* (rel. intensity) 161 (M^+, 60), 166 (23), 149 (100); $[\alpha]_D^{20}$ 177° (*c* 1.5, $CHCl_3$) (lit.[2] $[\alpha]_D^{20}$ 178° (*c* 1.0, $CHCl_3$).

(*S*)-(methoxycarbonyl)(phenyl)methyl 2-(2-iodophenyl)acetate (12). To a stirred solution of 2-iodophenylacetic acid (**1f**, 260 mg, 1 mmol), (+)-**11** (246 mg, 1.3 mmol, 1.3 equiv) and 4-dimethylaminopyridine (DMAP, 12 mg, 0.1 mmol, 0.1 equiv) in anhydrous CH_2Cl_2 (10 mL) was added *N,N'*-di-*iso*-propylcarbodiimide (DIC, 1.69 mL, 10.8 mmol, 1.8 equiv) at 0°C.

[1] Ebbers, E. J.; Ariaans, G.J. A.; Bruggink, A.; Zwanenburg, B. *Tetrahedron Asym.* **1999**, *10*, 3701–3718.
[2] Defoin, A.; Pires, J.; Tissot, I.; Tschamber, T.; Bur, D. *Tetrahedron Asym.* **1991**, *12*, 1209–1221.

The mixture was allowed to warm up to rt and left stirring overnight. The resulting suspension was filtered and the solid was washed with CH_2Cl_2. The filtrate was evaporated to give a residue, which was then suspended into Et_2O (5 mL). This suspension was filtered and the solid was washed with Et_2O (2 × 3 mL). The filtrates were washed with aq. 1 M HCl (2 × 5 mL) and brine (5 mL), dried over $MgSO_4$, filtered and evaporated to give a residue, which was purified by column chromatography (cyclohexane/EtOAc, 20:1) to furnish (+)-**12** (283 mg, 74 %) as a colorless oil. IR (neat) ν_{max} 3018, 2997, 2935, 1739, 1712, 1451, 1237, 1085 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.84 (d, J = 8.3 Hz 1H), 7.47-7.29 (m, 7H), 7.00-6.94 (m, 1H), 5.98 (s, 1H), 4.0 (d, J = 16.8 Hz, 1H), 3.93 (d, J = 16.8 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.9, 169.0, 193.5, 137.1, 133.6, 130.7, 129.2, 129.0, 128.7, 128.4, 127.6, 101.0, 74.8, 52.6, 45.8; EIMS *m/z* (rel. intensity) 410 (M^+, 31), 245 (24), 283 (57), 135 (100); HRMS (ESI) calcd for $C_{17}H_{15}IO_4Na$ ($[M+Na]^+$) 432.9913, found 432.988; $[\alpha]_D^{20}$ 111.7° (*c* 1.0, $CHCl_3$).

(*S*)-(methoxycarbonyl)(phenyl)methyl-2-(2-iodophenyl)butanoate (13d1/13d2). To a stirred solution of *t*-BuOK (407 mg, 3.6 mmol, 1.1 equiv) in anhydrous THF (30 mL) at -78°C was added (+)-**12** (1.35 g, 3.3 mmol) and, after 2 min, EtI (325 µl, 3.9 mmol, 1.2 equiv). The reaction mixture was allowed to warm up to rt, and stirring was continued until complete conversion of the starting material was observed by TLC (*ca*. 6h). Water (30 mL) was added and the mixture was extracted with Et_2O (3 × 40 mL). The organic layers were washed with sat. aq. NH_4Cl (50 mL) and brine (50 mL), dried over $MgSO_4$ and evaporated. The resulting residue was purified by column chromatography (cyclohexane/EtOAc, 20:1) to furnish the two expected diastereoisomers **13d1** (348 mg, 24 %) and **13d2** (395 mg, 27 %) as colourless oils. **13d1**: IR (neat) ν_{max} 3049, 2834, 1739, 1604, 1452, 1384, 1261, 1114, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.83 (d, J = 1.1, 8.0 Hz, 1H), 7.40-7.28 (m, 7H), 6.92 (t, J = 7.5 Hz, 1H), 5.90 (s, 1H), 4.18 (t, J = 7.3 Hz, 1H), 3.73 (s, 3H), 2.24-2.08 (m, 1H), 1.95-1.79 (m, 1H), 1.00 (d, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.9 (COO), 169.2 (COO), 141.4 (CH_{aro}), 139.7 (Cq_{aro}), 133.5 (CH_{aro}), 129.0 (CH_{aro}), 128.9 (CH_{aro}), 128.6 (CH_{aro} ×2), 128.5 (CH_{aro}), 128.0 (CH_{aro}), 127.4 (CH_{aro} ×2), 102.0 (C-I), 76.6 (CH), 74.7 (CH), 56.2 (CH_2), 52.6 (CH_3), 26.9 (CH_2), 11.9 (CH_3); EIMS *m/z* (rel. intensity) 438 (M^+, 3), 379 (9), 311 (25), 289 (61), 252 (41), 118 (11), 89 (100); HRMS (ESI) calcd for $C_{19}H_{19}O_4INa$ ($[M+Na]^+$) 461.0226, found 461.0221; $[\alpha]_D^{20}$ 77.3° (*c* 1.0, $CHCl_3$). **13d2**: IR (neat) ν_{max} 3052, 2834, 1738, 1611, 1450, 1381, 1261, 1117, 1101 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.89 (d,

J = 8 Hz, 1H), 7.37- 7.32 (m, 7H), 6.97 (td, J =1.9, 8 Hz, 1H), 5.92 (s, 1H, CH $_{benz.}$), 4.15 (t, J = 7.4 Hz, 1H), 3.61 (s, 3H), 2.20-2.05 (m, 1H), 1.78-1.93 (m, 1H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.6 (COO), 168.9 (COO), 141.4 (Cq $_{aro}$), 139.7 (Cq$_{aro}$), 133.6 (Cq$_{aro}$), 129.1 (CH$_{aro}$), 128.9 (CH$_{aro}$), 128.7 (CH$_{aro}$ × 2), 128.4 (CH$_{aro}$), 128.2 (CH$_{aro}$), 127.4 (CH$_{aro}$ × 2), 102.0 (C-I), 76.6 (CH), 74.7 (CH), 56.3 (CH_2), 52.4 (CH_3), 26.6 (CH_2), 11.9 (CH_3); EIMS m/z (rel. intensity) 438 (M^+,6), 311 (18), 289 (34), 252 (19), 89 (100); HRMS (ESI) calcd for $C_{19}H_{19}O_4INa$ ([M+Na]$^+$) 461.0226, found 461.0213; $[\alpha]_D^{20}$ 138.2° (c 1.0, $CHCl_3$)

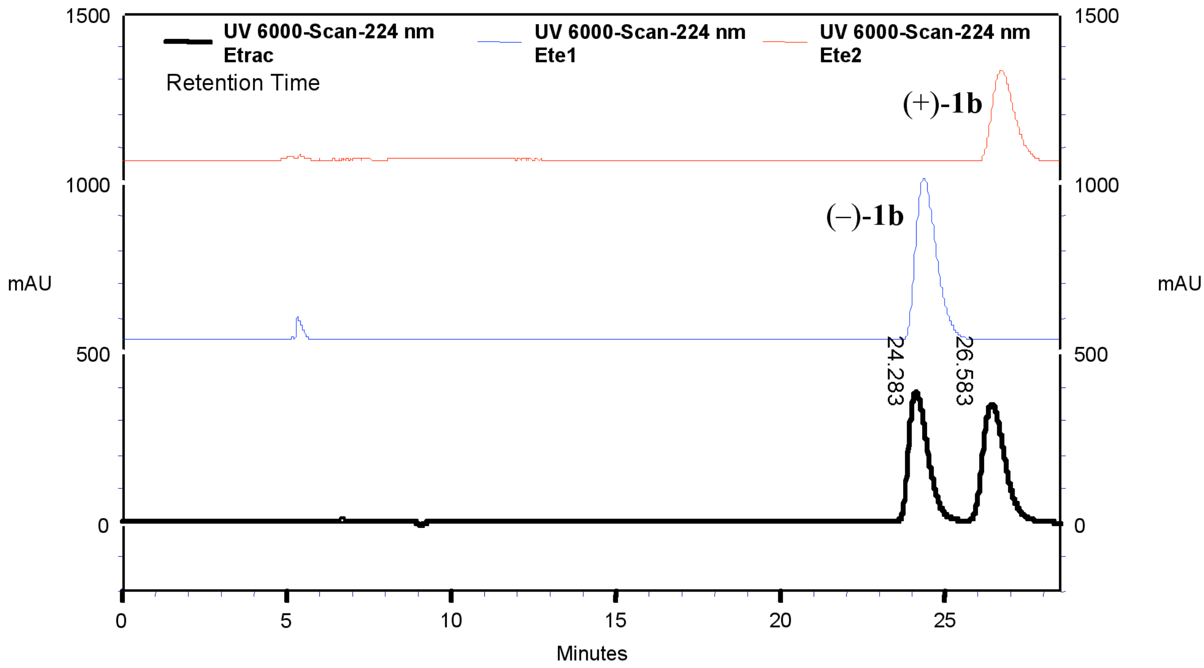
***(S)*-(methoxycarbonyl)(phenyl)methyl-2-(2-iodophenyl)-4-methylpentanoate (14d1/14d2)**. To a stirred solution of t-BuOK (410 mg, 3.6 mmol, 1.1 equiv) in anhydrous THF (30 mL) at –78 °C was added (+)-**12** (1.35 g, 3.3 mmol) and, after 2 min, i-BuI (449 µl, 3.9 mmol, 1.2 equiv). The reaction mixture was allowed to warm up to rt and stirring was continued until complete conversion of the starting material was observed by TLC (*ca*. 12h). Water (30 mL) was added and the mixture was extracted with Et_2O (3 × 40 mL). The organic layers were washed with sat. aq. NH_4Cl (50 mL) and brine (50 mL), dried over $MgSO_4$ and evaporated. The resulting residue was purified by column chromatography (cyclohexane/EtOAc, 20:1) to furnish the two separated diastereoisomers **14d1** (412 mg, 27 %) and **14d2** (435 mg, 28 %) as colourless oils. **14d1**: IR (neat) ν_{max} 3033, 3016, 2882, 1747, 1591, 1411, 1382, 1379, 1254, 1162, 1093 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.83 (d, J = 7.9 Hz 1H), 7.40-7.28 (m, 7H), 6.92 (t, J = 7.5 Hz, 1H), 5.89 (s, 1H), 4.34 (t, J = 7.5 Hz, 1H), 3.72 (s, 3H), 2.08-1.94 (m,1H), 1.73-1.57 (m, 2H), 1.01 (d, J = 6.2 Hz, 3H), 0.96 (d, J = 6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.0 (COO), 169.1 (COO), 141.6 (Cq $_{aro}$), 139.8 (CH $_{aro}$), 133.6 (Cq $_{aro}$), 129.0 (CH $_{aro}$), 128.9 (CH $_{aro}$), 128.6 (CH $_{aro}$ x2), 128.5 (CH $_{aro}$), 128.0 (CH $_{aro}$), 127.3 (CH $_{aro}$ x2), 101.6 (C-I), 74.7 (OCH $_{benz}$), 52.9 (CH $_{benz}$), 52.6 (OCH_3), 42.5 (CH_2), 26.0 (CH), 22.8 (CH_3), 22.4 (CH_3); EIMS m/z (rel. intensity) 466 (M^+, 2), 407 (13), 339 (51), 317 (61), 193 (14), 190 (59), 89 (100); HRMS (ESI) calcd for $C_{21}H_{23}O_4NaI$ ([M+Na]$^+$) 489.0539, found 489.0525; $[\alpha]_D^{20}$ 92.0° (c 0.8, $CHCl_3$). **14d2**: IR (neat) ν_{max} 3030, 2887, 1741, 1586, 1418, 1386, 1257, 1163, 1091 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.89 (d, J = 7.9 Hz, 1H), 7.43- 7.31 (m, 7H), 6.96 (t, J = 7.5 Hz, 1H), 5.91 (s, 1H), 4.30 (t, J = 7.5 Hz, 1H), 3.58 (s, 3H), 2.04-1.94 (m, 1H), 1.74-1.57 (m, 2H), 0.95 (d, J = 3.2 Hz, 3H), 0.93 (d, J = 3.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.8 (COO), 168.8 (COO), 141.6 (Cq $_{aro}$), 139.8 (CH $_{aro}$), 133.6 (Cq $_{aro}$), 129.1 (CH $_{aro}$), 128.9 (CH $_{aro}$), 128.7(CH $_{aro}$ x2), 128.4 (CH $_{aro}$), 128.3 (CH $_{aro}$), 127.4 (CH $_{aro}$ x2), 101.7 (C-I), 74.7 (OCH $_{benz}$), 52.9 (CH $_{benz}$), 52.4

(OCH_3), 42.2 (CH_2), 26.0 (CH), 22.7 (CH_3), 22.5 (CH_3); EIMS m/*z* (rel. intensity) 466 (M^+, 7), 407 (22), 339 (79), 317 (88), 273 (31), 190 (46), 89 (100); HRMS (ESI) calcd for $C_{21}H_{23}O_4NaI$ ($[M+Na]^+$) 489.0539, found 489.0531; $[\alpha]_D^{20}$ 139.8° (*c* 1.0, $CHCl_3$).

(–)-2-(2-iodophenyl)butanoic acid (–)-1b. To a stirred solution of **13d1** (438 mg, 1 mmol) in THF (15 mL) was added a solution of $LiOH.H_2O$ (147 mg, 3.5 mmol) in water (5 mL) and 5 drops of H_2O_2 (35 wt.% in water). The reaction mixture was stirred for 3 h at rt and THF was evaporated. The resulting mixture was acidified to pH 1 with aq. HCl (10%), saturated with NaCl and extracted with EtOAc (3 × 10 mL). The organic layers were combined, washed with brine (10 mL), dried over $MgSO_4$, filtered, and evaporated to give a residue, which was purified by column chromatography (cyclohexane/EtOAc/AcOH, 6:1:0.1) to furnish pure (–)-**1b** (177 mg, 61%) as a white solid: mp = 64 °C; IR (neat) ν_{max} 3081, 2945, 2805, 2611, 2529, 1695, 1546, 1484, 1448, 1375, 1198 cm^{-1}; ^1H NMR ($CDCl_3$) δ 11.4 (brs, 1H, COOH), 7.87 (dd, *J* = 0.8, 7.9 Hz, 1H), 7.33-7.29 (m, 2H), 6.95 (ddd, *J* = 2.2 , 6.6, 10.2 Hz, 1H), 4.04 (t, *J* = 7.4 Hz, 1H), 2.15-2.01 (m, 1H), 1.90-1.75 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 179.7 (COO), 141.4 (Cq_{aro}), 139.8 (CH_{aro}), 129.0 (CH_{aro}), 128.6 (CH_{aro}), 127.9 (CH_{aro}), 102.0 (C-I), 56.4 (CH_{benz}), 26.5 (CH_2), 11.9 (CH_3); EIMS *m*/*z* (rel. intensity) 290 (M^+, 11), 245 (10), 163 (30), 89 (100); HRMS (ESI) calcd for $C_{10}H_{10}INa_2O_2$ (M+2Na-H) 334.9521, found 334.9534; $[\alpha]_D^{20}$ –73.9° (*c* 0.5, $CHCl_3$); HPLC analysis (column Chiralcel OJ-H, *n*-hexane/*iso*-propanol, 97:3, 0.5 mL/min, λ_{max} = 224 nm): Rt = 24.3 min.

(+)-2-(2-iodophenyl)butanoic acid (+)-1b. To a stirred solution of **13d2** (450 mg, 1.03 mmol) in THF (15 mL) was added a solution of $LiOH.H_2O$ (151 mg, 3.6 mmol) in water (5 mL) and 5 drops of H_2O_2 (35 wt.% in water). The mixture was stirred for 3 h at rt and THF was evaporated. The resulting mixture was acidified to pH 1 with aq. HCl (10%), saturated with NaCl and extracted with EtOAc (3 × 10 mL). The organic layers were combined, washed with brine (10 mL), dried over $MgSO_4$, filtered and evaporated to give a residue, which was purified by column chromatography (cyclohexane/EtOAc/AcOH, 6:1:0.1) to furnish pure (+)-**1b** (199 mg, 67%) as a white solid: mp = 64 °C; IR (neat) ν_{max} 3081, 2945, 2805, 2611, 2529, 1695, 1546, 1484, 1448, 1375, 1198 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 10.7 (brs, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.38-7.30 (m, 2H), 6.99-6.93 (m, 1H), 4.04 (t, *J* = 7.3 Hz, 1H), 2.13-2.03 (m, 1H), 1.87-1.77 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.5 (COO), 141.3 (Cq_{aro}), 139.8 (CH_{aro}), 129.0 (CH_{aro}), 128.6 (CH_{aro}), 127.9 (CH_{aro}), 102.0 (C-I), 56.3 (CH_{benz}), 26.5 (CH_2), 11.9 (CH_3); EIMS *m*/z (rel. intensity) 290 (M^+, 9), 245 (12),

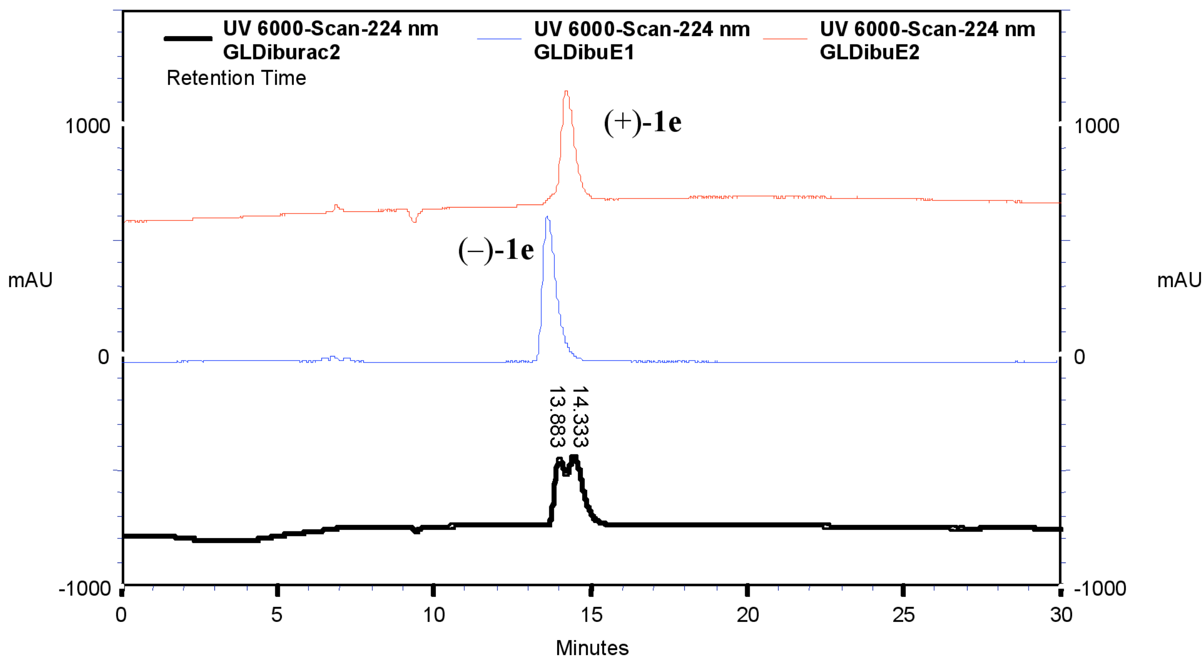
194 (49), 163 (27), 89 (100); HRMS (ESI) calcd for $C_{10}H_{10}INa_2O_2$ ($[M+2Na-H]^+$) 334.9521, found 334.9513; $[\alpha]_D^{20}$ 87.1° (*c* 0.6, $CHCl_3$); HPLC analysis (column Chiralcel OJ-H, *n*-hexane/*iso*-propanol, 97:3, 0.5 mL/min, λ_{max} = 224 nm): Rt = 26.6 min.



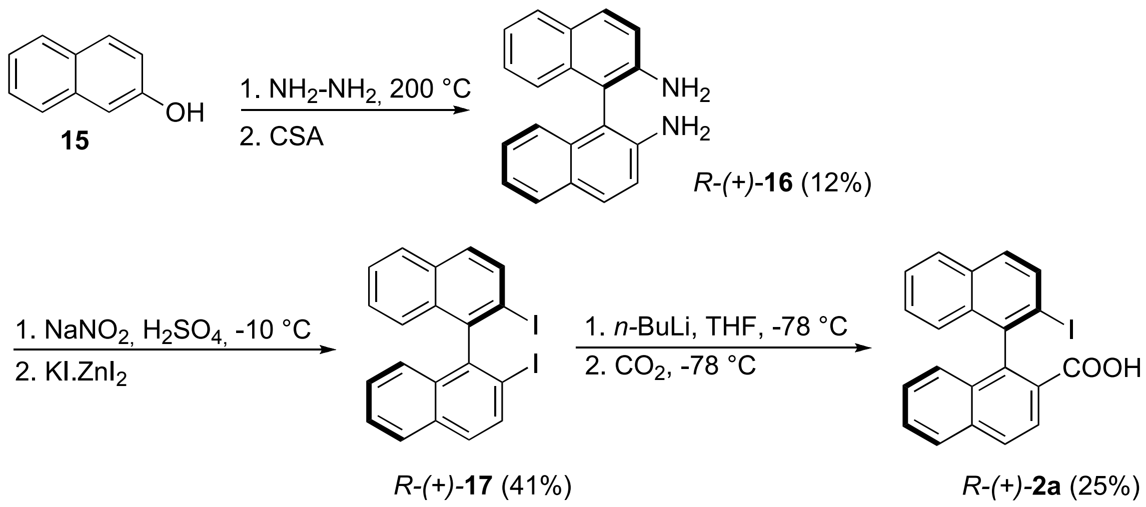
(–)-2-(2-iodophenyl)-4-methylpentanoic acid (–)-1e. To a stirred solution of **14d1** (466 mg, 1.0 mmol) in THF (15 mL) was added a solution of $LiOH.H_2O$ (147 mg, 3.5 mmol) in water (5 mL) and 5 drops of H_2O_2 (35 wt.% in water). The mixture was stirred for 3 h at rt and THF was evaporated. The resulting mixture was acidified to pH 1 with aq. HCl (10%), saturated with NaCl and extracted with EtOAc (3 × 10 mL). The organic layers were combined, washed with brine (10 mL), dried over $MgSO_4$ and evaporated to give a residue, which was purified by column chromatography (cyclohexane/EtOAc/AcOH, 6:1:0.1) to furnish pure (–)-**1e** (235 mg, 74%) as a colorless oil. IR (neat) ν_{max} 3033, 2918, 2850, 2674, 1801, 1640, 1594, 1502, 1467, 1375, 1274, 1205 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 10.57 (brs, 1H, COOH), 7.85 (dd, J = 0.9, 7.9 Hz, 1H), 7.39-7.29 (m, 2H), 6.95 (ddd, J = 2.0, 7.2, 9.0 Hz, 1H), 4.18 (t, J = 7.2 Hz , 1H), 1.99-1.89 (m, 1H), 1.69-1.51 (m, 2H), 0.96 (d, J = 4.9 Hz, 3H), 0.94 (d, J = 4.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.5 (COO), 141.6 (Cq_{aro}), 139.8 (CH_{aro}), 129.0 (CH_{aro}), 128.6 (CH_{aro}), 128.0 (CH_{aro}), 101.7 (C-I), 53.0 (CH_{benz}), 42.3 (CH), 26.0 (CH), 22.7 (CH_3), 22.5 (CH_3); EIMS *m*/*z* (rel. intensity) 318 (M^+, 37), 262 (52), 260 (19), 259 (62), 274 (24), 191 (81), 171 (46), 135 (100); HRMS (ESI) calcd for $C_{12}H_{15}IO_2Na_2$ ($[M+2Na-H]^+$) 362.9834, found 362.9840; $[\alpha]_D^{20}$ –94.8° (*c* 1.0, $CHCl_3$); HPLC

analysis (column Chiralcel OJ-H, *n*-hexane/*iso*-propanol, 97:3, 0.5 mL/min, λ_{max} = 224 nm): Rt = 13.9 min.

(+)-2-(2-iodophenyl)-4-methylpentanoic acid (+)-1e. To a stirred solution of **14d2** (500 mg, 1.07 mmol) in THF (16 mL) was added a solution of LiOH.H_2O (157 mg, 3.75 mmol) in water (5 mL) and 5 drops of H_2O_2 (35 wt.% in water). The mixture was stirred for 3 h at rt and THF was evaporated. The resulting mixture was acidified to pH 1 with aq. HCl (10%), saturated with NaCl and extracted with EtOAc (3 × 10 mL). The organic layers were combined, washed with brine (10 mL), dried over $MgSO_4$ and evaporated to give a residue, which was purified by column chromatography (cyclohexane/EtOAc/AcOH, 6:1:0.1) to furnish pure (+)-**1e** (245 mg, 72%) as a colorless oil. IR (neat) ν_{max} 3033, 2918, 2850, 2674, 1801, 1640, 1594, 1502, 1467, 1375, 1274, 1205 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.85 (d, J = 8.0 Hz, 1H), 7.39-7.29 (m, 2H), 6.97-6.92 (m, 1H), 4.18 (t, J = 7.5 Hz , 1H), 1.99-1.89 (m, 1H), 1.69-1.51 (m, 2H), 0.97-0.92 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.5 (COO), 141.6 (Cq), 139.8 (CH), 129.0 (CH), 128.6 (CH), 128.0 (CH), 101.7 (Cq-I), 53.0 (CH_{benz}), 42.3 (CH), 26.0 (CH), 22.7 (CH_3), 22.5 (CH_3); EIMS *m/z* (rel. intensity) 318 (M^+, 21), 262 (12), 259 (29), 191 (27), 134 (33), 89 (100); HRMS (ESI) calcd for $C_{12}H_{15}IO_2Na_2$ ([M+2Na-H]$^+$) 362.9834, found 362.9847; $[\alpha]_D^{20}$ 99.9° (*c* 1.0, $CHCl_3$); HPLC analysis (column Chiralcel OJ-H, *n*-hexane/*iso*-propanol, 97:3, 0.5 mL/min, λ_{max} = 224 nm): Rt = 14.3 min.



Preparation of 2a



***(R)-(+)*-2,2'-diamino-1,1'-binaphthyl [DABN, (16)].**[3] Monohydrate hydrazine (4.9 mL, 0.1 mol) and 2-naphthol **15** (29 g, 0.2 mol) are mixed and the mixture was heated at 190-220 °C for 85 h. The resulting mixture was then cooled down to about 60 °C, diluted into MeOH and acidified with 20% (v/v) conc. HCl (37%) (300 mL). To the resulting brownish solution was then added Et_2O until complete precipitation of a solid that was recovered by filtration. The solid was then dissolved into EtOAc (300 mL) and an aqueous 1 M solution of NaOH (100 mL). After separation, the aqueous layer was extracted with Et_2O (2 × 50 mL). The organic layers were combined, dried over Na_2SO_4 and evaporated to give *rac*-DABN (*rac*-**16**, 8.52 g). *D*-10-camphosulfonic acid (6.9 g, 0.03 mol) was dissolved in hot degassed ethanol (9 mL) at 50-60 °C. The resulting solution was cooled down to rt, water was added (5 mL) and a solution of *rac*-**16** (8.5 g, 0.03 mol) in CH_2Cl_2 (100 mL) was slowly added via a syringe with gentle stirring. The resulting suspension was left standing for 24 h in the dark. The resulting salt was filtered, washed with CH_2Cl_2 and dissolved in EtOAc (300 mL) and an aqueous 1 M solution of NaOH (100 mL) was added. After separation, the aqueous layer was further extracted with EtOAc (2 × 50 mL). The organic layers were combined, dried over Na_2SO_4 and evaporated to give *(R)*-(+)-**16** (2.69 g, 12 %) as a pinkish white powder: mp = 218-220 °C (lit.[3] mp = 244.5-247 °C); IR (neat) ν_{max} 1620, 812 cm^{-1}; ^1H NMR (DMSO-d_6, 250 MHz) δ 7.77-7.74 (m, 4H), 7.22 (d, J = 9.0 Hz, 2H), 7.12-7.08 (m, 4H), 6.80-6.76 (m, 2H), 4.64 (s, 4H); ^{13}C NMR (DMSO-d_6, 75,5 MHz) δ 141.9 (Cq (NH_2)), 131.5 (Cq), 126.5 (Cq), 125.9 (CH), 125.2 (CH), 123.9 (CH), 121.1 (CH), 118.9 (CH), 116.5 (CH), 108.3 (Cq);

[3] Brown, K. J.; Berry, M. S.; Murdoch, J. R. *J. Org. Chem* **1985**, *50*, 4345–4349.

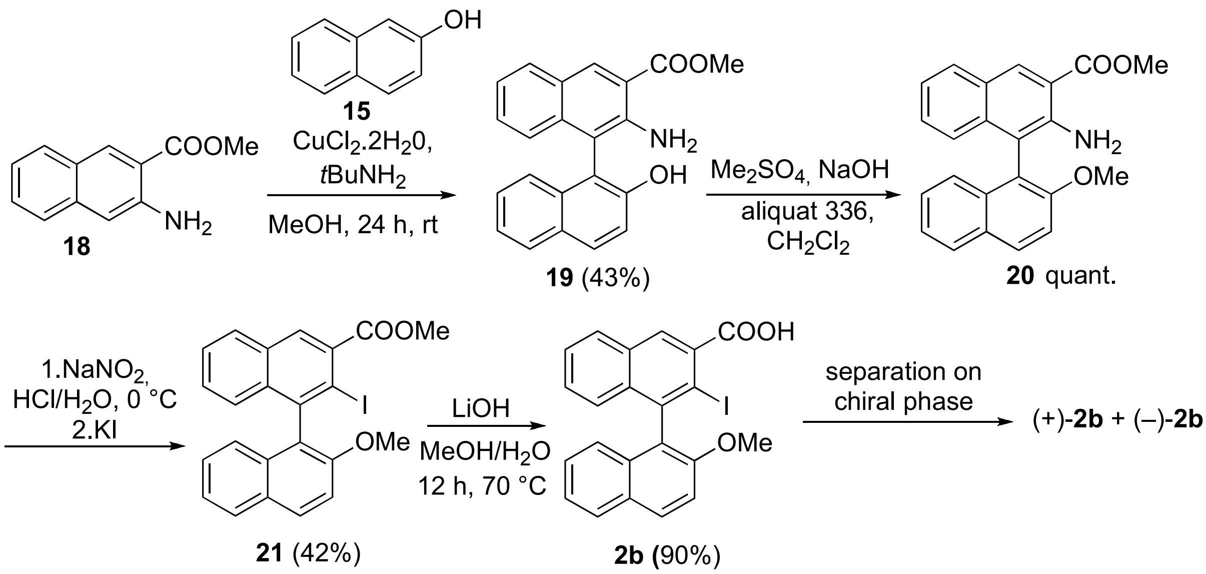
EIMS *m/z* (rel. intensity) 284 (M^+, 85), 268 (11), 143 (100), 115 (40); $[\alpha]^{20}_D$ 141° (*c* 1.00, pyridine) [lit.[3] $[\alpha]^{20}_D$ 155.5° (*c* 1.00, pyridine)].

***(R)*-(+)-2,2'-diiodo-1,1'-binaphthyl [DIBN, (+)-17)].**[3] To a solution of conc. H_2SO_4 (130 mL) at –10 °C was added portionwise $NaNO_2$ (3.8 g, 0.055 mol). The resulting suspension was allowed to warm up to rt until a complete dissolution was observed and then cooled down again to –10 °C. A solution of *(R)*-(+)-**16** (3.3 g, 0.011 mol) in pyridine (23 mL) was slowly added and the resulting mixture was stirred at –10 °C for 2 h. Ice was regularly added to the mixture during 1h and, 30 min later, an ice-cooled aqueous solution of urea (3.3 g, 0.033 mol, 82 mL) was slowly added to the reaction mixture, which had been first transferred into a large Erlenmeyer flask at 0 °C. This addition of urea caused an abundant foam formation. To this mixture was added an aqueous solution of ZnI_2 (10.4 g, 0.033 mol) and KI (16.5 g, 0.099 mmol) (32 mL). After filtration of the resulting brownish suspension, the brown solid was triturated with Et_2O and the resulting red filtrate was discoloured by washing with a saturated aqueous solution of sodium bisulfite, dried over Na_2SO_4 and evaporated to give a residue, which was purified by column chromatography, eluting with cyclohexane, to furnish pure (+)-**17** (2.3 g, 41%) as an orange solid: mp = 206-207 °C (lit.[3] 215-217 °C); IR (neat) ν_{max} 2970, 1459, 812 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.07 (d, J = 8.9 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.54-7.48 (m, 2H), 7.33-7.26 (m, 2H), 7.10 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 62,9 MHz) δ 145.1 (Cq), 136.0 (CH), 133.4 (Cq), 130.1 (CH), 128.6 (CH), 127.7 (CH), 126.9 (CH), 126.7 (CH), 100.1 (Cq); EIMS *m/z* (rel. intensity) 506 (M^+, 13), 252 (100); $[\alpha]^{20}_D$ 17° (*c* 1.72, pyridine) [lit.[3] $[\alpha]^{23}_D$ 16.4° (*c* 1.72, pyridine)].

***(R)*-(+)-2'-iodo-1,1'-binaphthalenyl-2-carboxylic acid (2a).** To a solution of (+)-**17** (100 mg, 0.190 mmol) in anhydrous THF (1.5 mL) was rapidly added a solution of *n*-BuLi (1.6 M, 0.119 mL) at –78 °C. After 20 min of stirring, bubbling of carbone dioxyde through the reaction mixture was started and the mixture was allowed to warm up to rt with continuous stirring until complete conversion of the starting material was observed by TLC (cyclohexane). Et_2O (20 mL) was added and the resulting mixture was extracted with an aqueous 1 M solution of NaOH (3 × 20 mL). The aqueous layers were combined, acidified with 1 M HCl (*ca*. 60 mL) and extracted with Et_2O (3 × 20 mL). These organic layers were combined, washed with brine, dried over Na_2SO_4 and evaporated to give a residue, which was purified by column chromatography (CH_2Cl_2/MeOH, 40:1) to furnish pure **2a** (20 mg,

25%) as a colourless and viscous oil. IR (neat) ν_{max} 3061, 1693 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.19-8.09 (m, 3H), 8.02 (t, J = 8.8 Hz, 2H), 7.80 (d, J = 8.8 Hz, 1H), 7.62 (t, J = 7.1 Hz, 1H), 7.50 (t, J = 7.1 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.26 (t, J = 7.3 Hz, 1H), 6.92 (d, J = 8.8 Hz, 1H), 6.87 (d, J = 8.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 177.0 (Cq), 153.2 (Cq),152.7, 146.0, 145.9, 144.3, 143.3, 142.5, 139.5, 139.1, 138.7, 138.6, 138.4, 137.6, 137.3, 137.3, 137.0, 136.9, 136.7, 108.8 (C-I); ESIMS *m/z* (rel. intensity) 424 (M$^+$, 71), 298 (100); HRMS (EI) calcd for $C_{21}H_{13}O_2I$ 423.9960, found 423.9939; $[\alpha]^{20}_D$ +3° (c 0.128, CH_2Cl_2).

Preparation of 2b



2’-Amino-3’-(methoxycarbonyl)-2-hydroxy-1,1’-binaphthalene (19).[4] To a solution of $CuCl_2.2H_2O$ (2.54 g, 0.015 mol) in MeOH (20 mL) was added a solution of *t*-butylamine (6.34 mL, 0.69 mol) in MeOH (20 mL). After 10 min of stirring at rt, a solution of 2-naphthol **15** (716 mg, 5 mmol) and methyl 3-aminonaphthalene-2-carboxylate **18** (1 g, 5 mmol) in MeOH (10 mL) was added. Stirring was continued at rt for 24 h, after which time the reaction mixture was acidified with conc. HCl (37%), then basified with aq. NH_4OH (30%). H_2O (100 mL) was added and the resulting deep blue aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The organic layers were combined, dried over Na_2SO_4 and evaporated to give a residue, which was purified by column chromatography (toluene) to furnish **19** (726 mg, 43%) as a yellow solid: mp = 154 °C (lit.[4] mp = 168-170 °C); IR (neat) ν_{max} 3486, 3375, 1698, 1619, 1596, 1563, 1207 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.63 (s, 1H), 7.88-7.73 (m, 3H), 7.30-

[4] Smrcina, M.; Vyskocil, S.; Maca, B.; Polasek, M.; Claxton, T. A. *J. Org. Chem.* **1994**, *59*, 2156–2163.

7.07 (m, 6H), 7.03 (d, J = 8.3 Hz, 1H), 6.86 (d, J = 7.9 Hz, 1H), 5.49 (s, 1H), 5.06 (s, 1H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.7 (Cq, COO), 152.4 (Cq), 145.6 (Cq), 137.2 (Cq), 135.5 (CH), 133.5 (Cq), 131.1 (CH), 130.3 (CH), 130.3 (Cq), 130.0 (CH), 128.8 (CH), 127.5 (Cq), 126.4 (CH), 124.7 (CH), 124.2 (CH), 123.9 (CH), 123.3 (CH), 118.3 (CH), 115.0 (Cq), 114.0 (Cq), 109.9 (Cq), 52.3 (CH_3); HRMS (ESI) calcd for $C_{22}H_{17}NO_3$ 343.12084, found 343.1229.

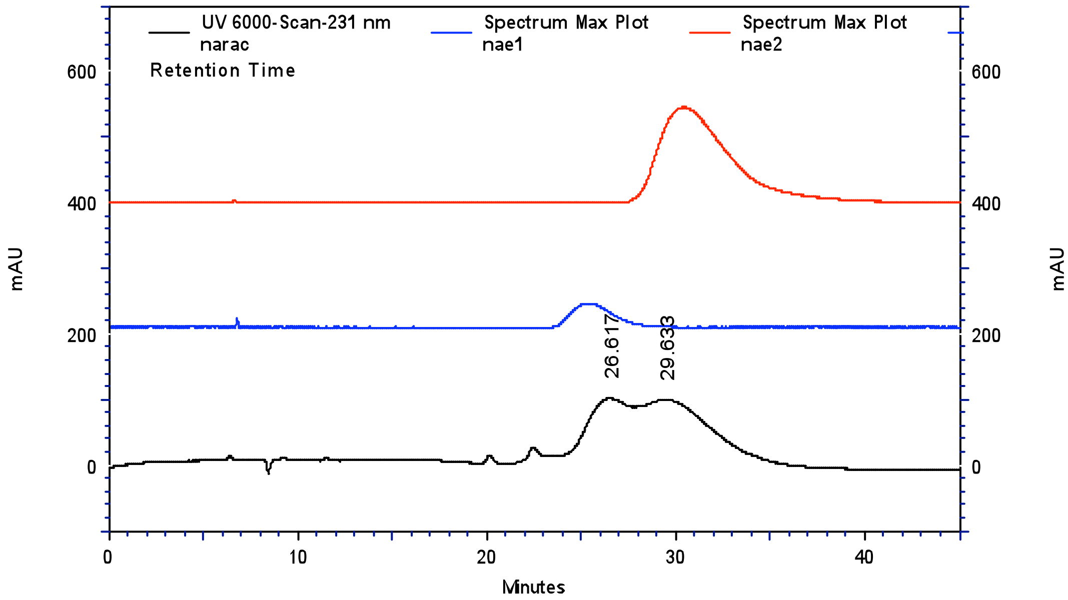
2'-Amino-3'-(methoxycarbonyl)-2-methoxy-1,1'-binaphthalene (20). To a solution of **19** (990 mg, 2.88 mmol) in CH_2Cl_2 (15 mL) was added an aqueous 1 M solution of NaOH (173 mg, 4.32 mmol, 15 mL), aliquat 336 (68 mg, 0.170 mmol) and dimethylsulfate (0.464 mL, 4.9 mmol). The resulting biphasic mixture was stirred at 40 °C for 5 h, after which time it was extracted with CH_2Cl_2 (3 × 15 mL), dried over Na_2SO_4 and evaporated to give **20** (1.03 g, quant.) as a yellow foam. IR (neat) ν_{max} 3378, 3055, 2951, 1697, 1208 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.84 (d, J = 9.1 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 7.1 Hz, 1H), 7.30 (d, J = 8.8 Hz, 1H), 7.19-7.02 (m, 5H), 6.71 (d, J = 7.6 Hz, 1H), 5.27 (s, 2H), 3.80 (s, 3H), 3.61 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.6 (Cq), 155.4 (Cq), 143.8 (Cq), 136.5 (Cq), 133.4 (CH), 130.2 (CH), 129.6 (CH), 128.7 (CH), 128.1 (CH), 127.0 (CH), 125.8 (Cq), 124.7 (CH), 124.0 (CH), 123.9 (CH), 122.1 (CH), 118.1 (Cq), 114.6 (Cq), 114.4 (Cq), 114.2 (CH), 56.7 (CH_3), 51.9 (CH_3); HRMS (ESI) calcd for $C_{23}H_{19}NO_3$ 357.1365, found 357.1371.

2-iodo-3-(methoxycarbonyl)-2'-methoxy-1,1'-binaphthalene (21). To a suspension of **20** (880 mg, 2.46 mmol) in conc. HCl (37%, 10 mL) and H_2O (10 mL) at 0 °C was slowly added via a syringe an aqueous solution of $NaNO_2$ (339 mg, 4.92 mmol, 5 mL). The resulting orange solution was stirred for 2 h at 0 °C and an aqueous solution of KI (4.08 g, 24.6 mmol, 16 mL) was then added. After heating at 60 °C for 1 h, EtOAc (20 mL) was added and heating was continued for 30 min. $Na_2S_2O_3$ was added until complete discoloration of the reaction mixture that was then extracted with EtOAc (3 × 50 mL). The organic layers were combined, washed with brine (50 mL), dried over Na_2SO_4, filtered and evaporated to give a residue, which was purified by column chromatography, eluting with toluene, to furnish pure **21** (486 mg, 42%) as a white solid: mp = 176°C; IR (neat) ν_{max} 1728, 1207 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.28 (s, 1H), 8.06 (d, J = 9.1 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.52 (td, J = 1.0, 8.0 Hz, 1H), 7.46 (d, J = 9.1 Hz, 1H), 7.38-7.17 (m, 4H), 6.95 (d, J = 8.3 Hz, 1H), 4.02 (s, 3H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.6 (Cq), 154.1 (Cq), 142.4 (Cq), 134.4 (Cq), 134.4 (Cq), 132.8 (Cq), 131.9 (Cq), 130.3 (CH), 130.0 (CH), 129.0 (Cq), 128.7

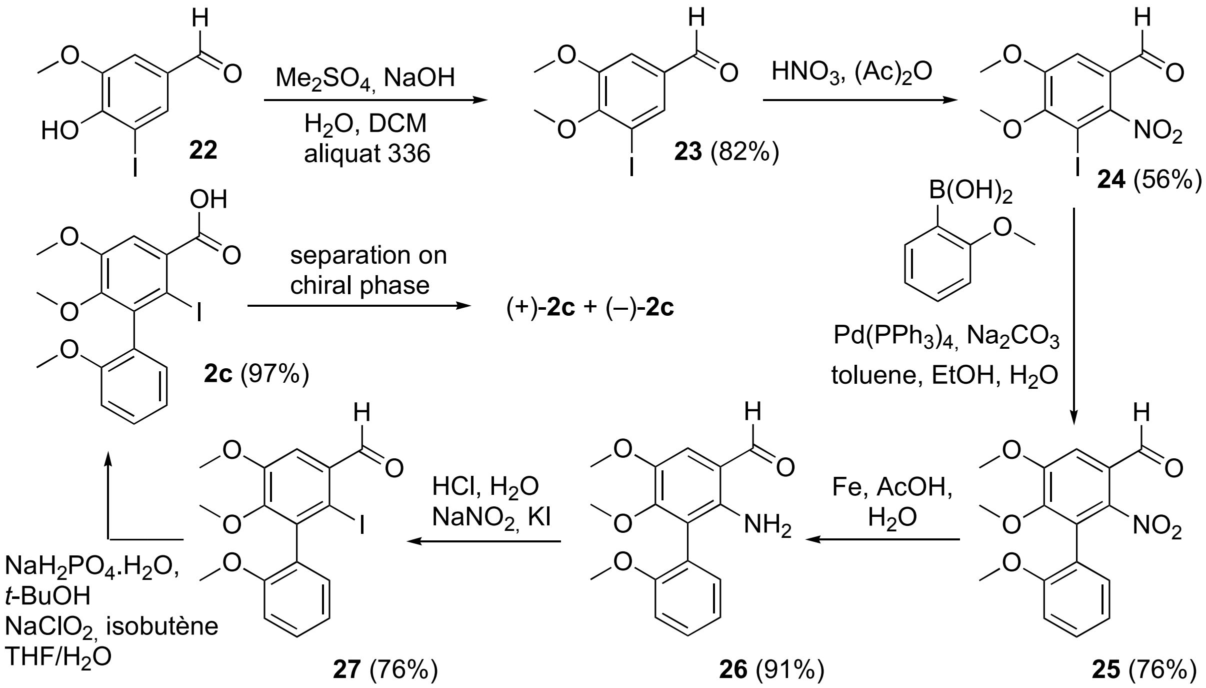
(CH), 128.7 (CH), 128.0 (CH), 127.1 (CH), 127.0 (CH), 126.9 (CH), 126.0 (Cq), 124.4 (CH), 123.8 (CH), 113.6 (CH), 97.6 (C-I), 56.5 (CH_3), 52.6 (CH_3); EIMS *m*/*z* (rel. intensity) 468 (M^+, 4), 469 (M^+, 1), 470 (M^+, 0.2), 28 (100); HRMS (ESI) calcd for $C_{23}H_{17}IO_3$ 468.0222, found 468.0241.

3-iodo-4-(2-methoxynaphthalen-1-yl)naphthalene-2-carboxylic acid (2b). To a suspension of **21** (400 mg, 0.85 mmol) in MeOH/H_2O (6:1, 70 mL) was added LiOH.H_2O (600 mg, 14 mmol). The reaction mixture was stirred at 70 °C for 12 h, after which time MeOH was evaporated and the resulting mixture was acidified with aq. 1 M HCl to pH 1, extracted with EtOAc (3 × 50 mL), dried over Na_2SO_4, filtered and evaporated to give a residue, which was purified by column chromatography (acetone/cyclohexane, 1:1) furnish pure **2b** (350 mg, 90%) as a white solid: mp = 181 °C; IR (neat) ν_{max} 3457, 1699, 1267 cm^{-1}; ^{1}H NMR (DMSO-*d*^{6}, 300 MHz) δ 8.17-8.13 (m, 2H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 9.1 Hz, 1H), 7.65 (d, *J* = 9.2 Hz, 1H), 7.55 (t, *J* = 7.1 Hz, 1H), 7.38-7.23 (m, 3H), 6.95 (d, *J* = 8.5 Hz, 1H), 6.75 ((d, *J* = 8.3 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (DMSO-*d*^{6}, 100 MHz) δ 169.7 (COOH), 153.9 (Cq), 141.4 (Cq), 136.8 (Cq), 133.3 (Cq), 132.3 (Cq), 131.8 (CH), 130.4 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.2 (CH), 128.2 (CH), 127.1 (CH), 126.9 (Cq), 126.2 (CH), 124.9 (CH), 123.7 (CH), 114.0 (CH), 98.3 (C-I), 56.2 (CH_3); EIMS *m*/*z* (rel. intensity) 454 (M^+, 11), 429 (31), 327 (6), 282 (64), 28 (100); HRMS (ESI) calcd for $C_{22}H_{16}IO_3$ ($[M+H]^+$) 454.0144, found 454.0141; HPLC analysis (column Chiralcel OJ-H, *n*-hexane/*iso*-propanol, 95:5, 0.5 mL/min, λ_{max} = 231 nm): Rt = 26.6 and 29.6 min.

Separation of the two atropoisomers was performed on a Chiralcel OJ-H semi-preparative column (*n*-hexane/*iso*-propanol, 90:10, 10 mL/min, λ_{max} = 231 nm). 300 mg of the racemic mixture were separated to give (+)-**2b** (69 mg, 23%) and (–)-**2b** (84 mg, 28%). (+)-**2b**: $[\alpha]_D^{20}$ 79.9° (*c* 0.5, $CHCl_3$), Rt = 26.6 min; (–)-**2b**: $[\alpha]_D^{20}$ –85.5° (*c* 0.6, $CHCl_3$), Rt = 29.6 min.



Preparation of 2c



3-Iodo-4,5-dimethoxybenzaldehyde (23). To a solution of 4-hydroxy-3-iodo-5-methoxybenzaldehyde (**22,** 2.78 g, 10 mmol) in CH_2Cl_2/aq. 2 M NaOH (1:1, 90 mL) is added aliquat 336 (280 mg, 0.7 mmol) and dimethylsulfate (2 mL, 20 mmol). The mixture is stirred at rt for 3 h, after which time it was separated, the aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were evaporated to give residue, which was diluted in Et_2O, washed with aq. 2 M NH_4OH, aq. 2 M HCl and brine, dried over $MgSO_4$, filtered and

evaporated to give a residue, which was purified by column chromatography (CH_2Cl_2/cyclohexane, 4:3) to furnish **23** (1.994 g, 82%) as a white solid: mp = 69 °C (lit.[5] mp = 69-70°C); IR (neat) ν_{max} 2967, 2852, 2841, 1698, 1635, 1596, 1513, 1472, 1396, 1381, 1279, 1187, 1173, 1074 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.83 (s, 1H), 7.85 (d, J = 1.7 Hz, 1H), 7.41 (d, J = 1.7 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.6 (CH), 154.0 (Cq), 152.9 (Cq), 134.4 (CH), 133.8 (Cq), 111.0 (CH), 92.1 (C-I), 60.6 (CH_3), 56.0 (CH_3); EIMS m/z (rel. intensity) 292 (M^+, 31), 165 (100).

3-Iodo-4,5-dimethoxy-2-nitrobenzaldehyde (24).[6] To conc. nitric acid (40 mL) was added a solution of **23** (1.643 g, 5.6 mmol) in anhydride acetic acid (74 mL) at 0 °C. The mixture was stirred under reflux (85°C) for 2 h, then cooled down to rt and poured over ice. The resulting precipitate was filtered and washed with water (3 × 10 mL) to give a residue, which was purified by column chromatography (CH_2Cl_2/cyclohexane, 3:5) to furnish pure **24** (1.058 g, 56%) as a white solid: mp = 152 °C (lit.[6] mp = 153 °C); IR (neat) ν_{max} 2961, 2842, 2836, 1659, 1612, 1534, 1511, 1472, 1390, 1287, 1177, 1161, 1069 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.79 (s, 1H), 7.46 (s, 1H), 4.00 (s, 3H), 3.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.0 (CH), 154.4 (Cq), 153.3 (Cq),153.1 (Cq), 124.6 (Cq), 111.8 (CH), 87.1 (C-I), 61.1 (CH_3), 56.6 (CH_3); EIMS m/z (rel. intensity) 337 (M^+, 9), 210 (64), 193 (100).

3-(2-Methoxyphenyl)-4,5-dimethoxy-2-nitrobenzaldehyde (25). To a solution of 2-methoxyphenylboronic acid (1.00 g, 6.60 mmol) and **24** (2.00 g, 5.93 mmol) in degassed toluene/ethanol/aq. 2 M Na_2CO_3 (80 mL, 3:1:1) was added $Pd(PPh_3)_4$ (347 mg, 0.3 mmol). The stirred mixture was heated at 80 °C under Ar for 12 h. Additional amounts of 2-methoxyphenylboronic acid (304 mg, 2 mmol) and $Pd(PPh_3)_4$ (347 mg, 0.3 mmol) were then added and the reaction mixture was further stirred at 80 °C for 8 h, after which time it was hydrolyzed saturated aq. NH_4Cl (30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (70 mL), dried over $MgSO_4$, filtered and evaporated. The residue was purified by column chromatography (CH_2Cl_2/petroleum ether, 5:1) to furnish **25** (1.423 g, 76%) as a yellow solid, together with starting **24** (623 mg). **25**: mp = 151 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.93 (s, 1H), 7.50 (s, 1H), 7.40 (td, J = 1.7, 8 Hz, 1H), 7.16 (dd, J = 1.7, 7.4 Hz, 1H), 7.02 (d, J = 7.4 Hz, 1H), 6.98 (t, J = 8 Hz, 1H), 4.01 (s, 3H), 3.76 (s, 3H), 3.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 186.3 (C=O), 156.7 (Cq),

[5] Raiford; W. *J. Am. Chem. Soc.* **1935**, *57*, 2500–2502.
[6] Heacock, R. A.; Hutzinger, O.; Scott, B. D.; Daly, J. W.; Witkop, B. *J. Am. Chem. Soc.* **1963**, *85*, 1825–1831.

154.5 (Cq), 152.1 (Cq), 130.5 (CH aro), 130.4 (CH aro), 130.3 (Cq), 127.4 (Cq), 123.9 (Cq), 120.6 (CH aro), 120.2 (Cq), 110.9 (CH aro), 110.1 (CH aro), 61.0 (OCH_3), 56.4 (OCH_3), 55.5 (OCH_3); EIMS *m*/*z* (rel. intensity) 317 (M^+, 13), 288 (46), 286 (21), 271 (54), 189 (100); HRMS (ESI) calcd for $C_{16}H_{16}NO_6$ ($[M+H]^+$) 318.0972, found 318.0978.

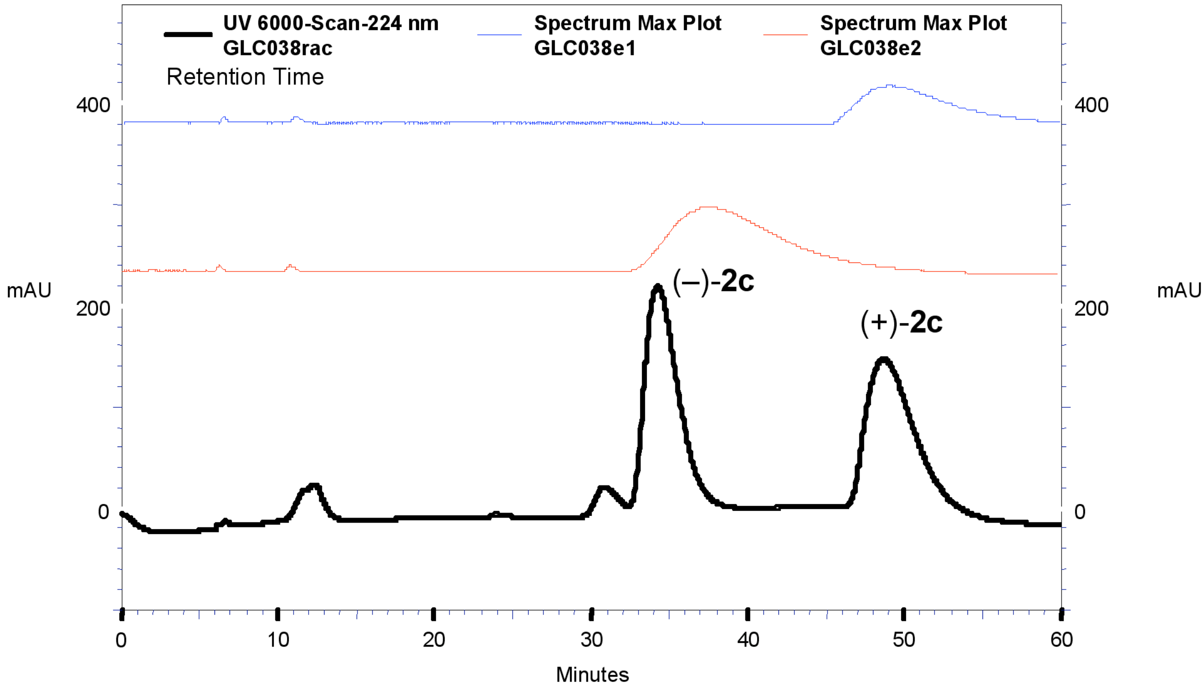
3-(2-Methoxyphenyl)-4,5-dimethoxy-2-aminobenzaldehyde (26). To a stirred suspension of **25** (630 mg, 2 mmol) in water (6 mL) was added AcOH (77 µl) and Fe (736 mg). The mixture was stirred at reflux for 3 h, after which time it was neutralized by addition of saturated aq. $NaHCO_3$ (5 mL). The mixture was then extracted with EtOAc (2 × 30 mL), and the combined organic layers were dried over $MgSO_4$, filtered and evaporated. The resulting crude product was triturated with petroleum ether (3 mL), filtered and the remaining solid was further washed with petroleum ether (2 × 1 mL) to furnish **26** (523 mg, 91%) as a yellow solid: mp = 113-114 °C; IR (neat) ν_{max} 3117, 3047, 2862, 2837, 2719, 1690, 1576, 1502, 1366, 1352 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.79 (s, 1H), 7.41 (ddd, J = 1.9, 7.4, 8.3 Hz, 1H), 7.16 (dd, J = 1.7, 7.4 Hz, 1H), 7.08 (dd, J = 0.9, 7.4 Hz, 1H), 7.06-7.01 (m, 2H), 3.87 (s, 3H), 3.77 (s, 3H), 3.67 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.0 (CHO), 157.4 (Cq), 154.4 (Cq), 145.1 (Cq), 144.1 (Cq), 131.8 (CH), 129.8 (CH), 121.8 (Cq), 121.2 (CH), 118.9 (CH), 117.7 (CH), 113.8 (Cq), 111.5 (CH), 60.6 (OCH_3), 56.6 (OCH_3), 55.6 (OCH_3); EIMS *m*/*z* (rel. intensity) 287 (M^+, 100), 272 (49), 256 (12), 244 (18), 241 (11), 226 (15), 212 (14); HRMS (ESI) calcd for $C_{16}H_{18}NO_4$ ($[M+H]^+$) 288.1236, found 288.1226.

3-(2-Methoxyphenyl)-4,5-dimethoxy-2-iodobenzaldehyde (27). To a stirred suspension of the aniline **26** (143 mg, 0.5 mmol) in water (2 mL) and conc. HCl (37%, 2 mL) was added a solution of $NaNO_2$ (69 mg, 1 mmol) in water (2 mL) at 0 °C. The resulting suspension was stirred at at 0 °Cfor 2 h, after which time a solution of NaI (750 mg, 5 mmol) in water (4.5 mL) was added and the reaction mixture was stirred at 60 °C for 3 h. The mixture was then neutralized by addition of saturated aq. $NaHCO_3$ (3 mL), treated with saturated aq. $Na_2S_2O_3$ (6 mL), and extracted with EtOAc (3 × 15 mL). The combined organic layers were dried over $MgSO_4$, filtered and evaporated to give a residue, which was purified by column chromatography (toluene) to furnish pure **27** (151 mg, 76 %) as a yellow solid, together with starting **26** (8 mg, 94 % conversion). **27**: mp = 163-164 °C; IR (neat) ν_{max} 3091, 3022, 2834, 2720, 1685, 1589, 1496, 1366, 1081 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 10.10 (s, 1H), 7.55 (s, 1H), 7.44 (ddd, J = 2.4, 7.0, 8.6 Hz, 1H), 7.01-6.99 (m, 3H), 3.95 (s, 3H), 3.78 (s, 3H), 3.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.6 (CHO), 156.6, 153.2, 152.6, 139.5, 131.5,

131.0, 129.8, 129.4, 120.6, 112.2, 111.1, 100.0 (C-I), 60.8 (OCH_3), 56.0 (OCH_3), 55.6 (OCH_3); EIMS *m/z* (rel. intensity) 398 (M^+, 52), 271 (58), 256 (100), 241 (35); HRMS (ESI) calcd for $C_{16}H_{16}O_4I$ ($[M+H]^+$) 399.0093, found 399.0074.

3-(2-Methoxyphenyl)-4,5-dimethoxy-2-iodobenzoic acid (2c). To a stirred suspension of **27** (200 mg, 0.5 mmol) in *t*-BuOH (12 mL) and H_2O (5 mL) was added $NaH_2PO_4.H_2O$ (276 mg, 2 mmol), a solution of 2-methylbutene in THF (1 M, 380 µl, 0.38 mmol) and $NaClO_2$ (272 mg, 3 mmol). The resulting solution was stirred at rt for 3 h, after which time it was evaporated to give a residue, which was purified by column chromatography (toluene/AcOH, 98:2) to furnish *rac*-**2c** (201 mg, 97 %) as a white solid: mp = 191 °C; IR (neat) ν_{max} 3012, 2917, 2778, 2509, 1686, 1596, 1419, 1263, 1187, 1057 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 11.7 (brs, 1H, COOH), 7.55 (s, 1H), 7.44 (ddd, J = 2.4, 7.0, 9.1 Hz, 1H), 7.01-6.99 (m, 3H), 3.95 (s, 3H), 3.78 (s, 3H), 3.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.7 (COOH), 156.5 (C-O), 152.3 (C-O), 150.3 (C-C), 140.7 (C-C), 130.8 (CH), 130.8 (CH), 130.0 (Cq), 129.5 (CH), 120.4 (CH), 114.8 (C-O), 111.0 (CH), 92.2 (C-I), 60.6 (OCH_3), 56.0 (OCH_3), 55.5 (OCH_3); EIMS *m/z* (rel. intensity) 414 (M^+, 17), 287 (17), 272 (100), 257 (39), 255 (26), 211 (31); HRMS (ESI) calcd for $C_{16}H_{15}O_5INa$ ($[M+Na]^+$) 436.9862, found 436.9865; HPLC analysis (column Chiralcel OJ-H, *n*-hexane/*iso*-propanol, 90:10, 0.5 mL/min, λ_{max} = 224 nm): Rt = 34.1 and 48.5 min

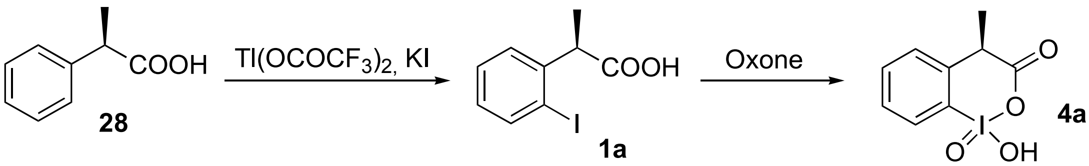
Separation of the two atropoisomers was performed on a Chiracel OJ-H semi-preparative column (*n*-Hexane/*iso*-propanol, 85:15, 10 mL/min, λ = 224 nm). 500 mg of the racemic mixture were separated to furnish (–)-**2c** (195 mg, 39%) and (+)-**2c** (197 mg, 39 %). (–)-**2c**: $[\alpha]_D^{20}$ –180.7° (*c* 0.6, $CHCl_3$); Rt = 34.1 min. (+)-**2c**: $[\alpha]_D^{20}$ 174.1° (*c* 0.6, $CHCl_3$); Rt = 48.5 min.



Preparation of Chiral Iodanes

Preparation of type 3 and 4 chiral iodanes

Preparation of the λ^5-iodane 4a from the iodoarene 1a



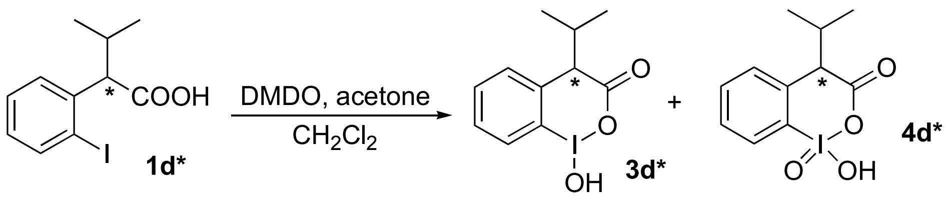
***(R)*-2-(2-iodophenyl)propanoic acid (1a).**[7] *(R)*-2-phenylpropanoic acid (**28**, 280 mg, 1.86 mmol) was dissolved in a solution of thallium trifluoroacetate (42% w/w, 2.4 g, 1.86 mmol) in TFA (2 mL) and the mixture was stirred at rt in the dark for 48 h. TFA was removed by co-evaporation with cyclohexane to give a solid, which was then suspended in an aqueous solution of KI (1.5 g, 9.3 mmol, 20 mL). The resulting black suspension was refluxed for 5 h, after which time sodium metabisulfite ($Na_2S_2O_5$, *ca.* 1 g) was added slowly until complete discoloration of the reaction mixture. The suspension was then heated at reflux for 30 min, filtered, and the solid was washed with acetone (2 mL). The filtrates were combined and extracted with Et_2O (3 × 10 mL). The organic layers were combined, dried over Na_2SO_4, filtered and evaporated to give a residue (775 mg), which was purified by column

[7] Taylor, E. C.; Kienzle, F.; Robey, R. L.; McKillop, A.; Hunt, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 4845–4850.

chromatography (CH_2Cl_2/MeOH, 40:1) to give a non-separable 1:1 mixture of **1a** and starting **28** (393 mg). **1a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 6.88 (d, J = 6.4 Hz, 1H), 6.77 (s, 1H), 3.99 (d, J = 6.6 Hz, 1H), 1.30 (d, J = 4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.1 (Cq), 141.8 (Cq), 138.7 (CH), 136.7 (CH), 128.6 (CH), 127.9 (CH), 100.1 (Cq), 48.5 (CH), 16.9 (CH_3).

(*R*)-2-(2-iodoxyphenyl)propanoic acid (4a).[8] The 1:1 mixture of **1a** and **28** (393 mg) was added to an aqueous solution of oxone (1.70 g, 5.58 mmol, 13 mL). The resulting suspension was stirred at 70 °C for 3 h. The mixture was then cooled down to 0 °C for 1 h and filtered. The solid was washed with CH_2Cl_2 to remove intact **28** and dried to give **4a** (175 mg, 62%) as a white solid: mp = 140 °C (violent decomposition!); IR (KBr): 3244, 1625, 741 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.73-7.71 (m, 1H), 7.71-7.32 (m, 2H), 7.23 (s, 1H), 4.39 (s, 1H), 1.2 (d, J = 6,6 Hz, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 174.8 (Cq), 149.5 (Cq), 139.9 (Cq), 132.0 (CH), 127.9 (CH), 127.7 (CH), 127.0 (CH), 41.0 (CH), 16.3 (CH_3); EIMS *m/z* (rel. intensity) 276 ([M-O_2]$^+$, 5), 231 (100), 149 (46); HRMS (EI) calcd for $C_9H_9IO_2$ ([M-O_2]$^+$), 275.9647, found 275.9654; $[\alpha]^{20}_D$ −166° (*c* 0.06, DMSO)

Preparation of the iodanes 3d and 4d from each iodoarene 1d enantiomer



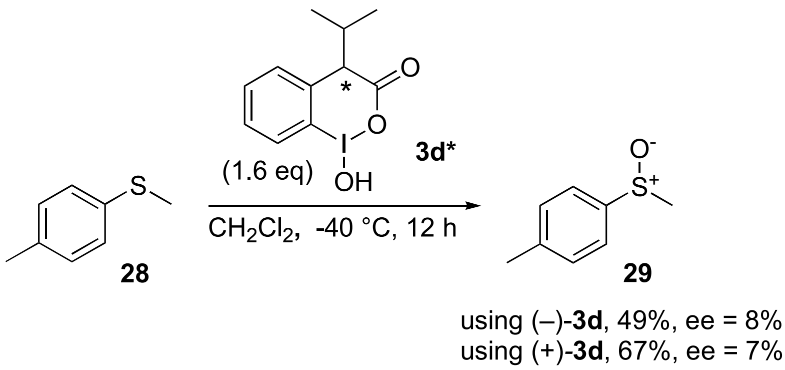
Oxidation of (+)-1d using DMDO in acetone.[9] A freshly prepared and titrated solution of dimethyldioxirane (DMDO) in acetone (0.1 M, 90 mL, 9 mmol) was added at 0 °C to a stirred solution of (+)-**1d** (912 mg, 3 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred at rt for 12 h and then evaporated. The residue was treated again twice with fresh solutions of DMDO in acetone (0.07 M, 130 mL, 9 mmol; 0.08 M, 110 mL, 9 mmol). After the third treatment, the resulting suspension was filtered and the solid was washed with Et_2O (10 mL) and CH_2Cl_2 (3 × 5 mL) to furnish **4d$_1$** (413 mg, 41%) as a white solid: mp > 250 °C (decomposition with emission of purple vapors); IR (KBr) ν_{max} 3277, 2984, 1712, 1367 cm^{-1};

[8] Frigerio, M.; Santagostino, M.; Sputore, S. *J. Org. Chem.* **1999**, *64*, 4537–4538.
[9] Murray, R. W.; Singh, M. *Org. Synt.* **1998**, *9*, 288–293.

NMR (DMSO-d^6): *insoluble in DMSO, as well as in D_2O*; Anal. Calcd for $C_{11}H_{13}IO_4$: C, 39.31; H, 3.90; I, 37.76; O, 19.04. Found: C, 40.32; H, 3.83; I, 37.65; O, 18.20. The filtrates were combined, evaporated and the resulting residue was dissolved in acetone (20 mL). Addition of petroleum ether afforded a precipitate, which was recovered by filtration and washed with petroleum ether (3 × 5 mL) to furnish (+)-**3d** (489 mg, 51%) as a white solid: mp = 212 °C (decomposition with emission of purple vapors); IR (KBr) ν_{max} 3146, 2975, 1707, 1361, 1217, 1085 cm^{-1}; ^1H NMR (DMSO-d^6, 300 MHz) δ 8.01-7.99 (m, 1H, CH $_{aro}$), 7.52-7.46 (m, 2H, CH $_{aro}$), 7.39-7.36 (m, 1H), 3.17 (d, J = 11.2 Hz, 1H), 2.39-2.5 (m, 1H), 1.07 (d, J = 6.5 Hz), 0.73 (d, J = 6.5 Hz, 3H); ^{13}C NMR (DMSO-d^6, 100 MHz) δ 173.2 (COO), 140.1 (Cq $_{aro}$), 133.2 (CH $_{aro}$), 130.3 (CH $_{aro}$), 129.8 (CH $_{aro}$), 129.0 (CH $_{aro}$), 119.7 (C-IO), 61.4 (CH $_{benz.}$), 27.5 (CH), 21.2 (CH_3), 21.0 (CH_3); EIMS *m/z* (rel. intensity) 178 ($M+H^+$–IO, 100); Anal. Calcd for $C_{11}H_{13}IO_3$: C, 41.27; H, 4.09; I, 39.64; O, 14.99. Found: C, 41.31; H, 4.03; I, 39.60; O, 15.06; $[\alpha]_D^{20}$ 67.2° (*c* 1.0, DMSO).

Oxidation of (–)-1d using DMDO in acetone. A freshly prepared solution of DMDO in acetone (0.1 M, 120 mL, 12 mmol) was added at 0 °C to a stirred solution of (–)-**1d** (1.22 g, 4 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred at rt for 12 h and then evaporated. The residue was treated again twice with fresh solutions of DMDO in acetone (0.1 M, 120 mL, 12 mmol; 0.08 M, 150 mL, 12 mmol). After the third treatment, the resulting suspension was filtered and the solid was washed with Et_2O (13 mL) and CH_2Cl_2 (3 × 6 mL) to furnish **4d₂** (82 mg, 6%) as a white solid: mp > 250 °C (decomposition with emission of purple vapor); IR (KBr) ν_{max} 3281, 2982, 1713, 1369 cm^{-1}. NMR (DMSO-d^6): *insoluble in DMSO, as well as in D_2O*; Anal. Calcd for $C_{11}H_{13}IO_4$: C, 39.31; H, 3.90; I, 37.76; O, 19.04. Found: C, 40.27; H, 4.54; I, 35.05; O, 20.14. The filtrates were combined, evaporated and the resulting residue was dissolved in acetone (25 mL). Addition of petroleum ether afforded a precipitate, which was recovered by filtration and washed with petroleum ether (3 × 7 mL) to furnish (–)-**3d** (1.16 g, 91%) as a white solid: mp = 220 °C (decomposition with emission of purple vapor); IR (KBr) ν_{max} 3148, 2974, 1707, 1361, 1088 cm^{-1}; ^1H NMR (DMSO-d^6, 300 MHz) δ 8.02-7.99 (m, 1H, CH $_{aro}$), 7.97 (s, 1H, COOH), 7.54-7.46 (m, 2H), 7.39-7.35 (m, 1H), 3.17 (d, J = 11.0 Hz, 1H), 2.50-2.37 (m, 1H), 1.07 (d, J = 6.6 Hz, 3H), 0.73 (d, J = 6.4 Hz, 3H). ^{13}C NMR (DMSO-d^6, 100 MHz) δ 173.0 (COO), 140.1 (Cq $_{aro}$), 133.2 (CH $_{aro}$), 130.3 (CH $_{aro}$), 129.8 (CH $_{aro}$), 129.0 (CH $_{aro}$), 119.7 (C-IO), 61.3 (CH $_{benz.}$), 27.5 (CH), 21.2 (CH_3), 21.0 (CH_3); EIMS *m/z* (rel. intensity) 178.0 ($M+H^+$-IO, 100); HRMS (ESI) calcd for $C_{11}H_{14}IO_3$ 320.9979, found 320.9992; $[\alpha]_D^{20}$ –64.3° (*c* 1.1, DMSO).

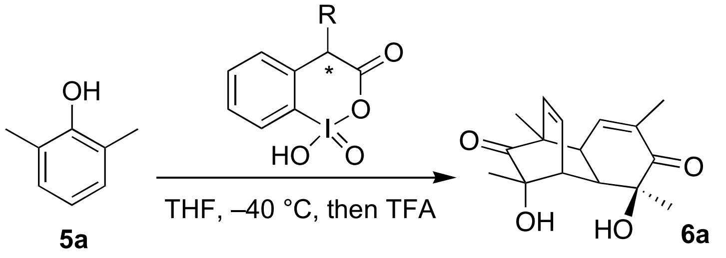
Preliminary Evaluation of the Reactivity and Enantioselectivity Induced by Chiral Iodanes of Types 3 and 4



Methyl-*p*-tolylsulfoxide (29). To a stirred solution of methyl-*p*-tolylsulfide (**28**, 138 mg, 1 mmol) in CH_2Cl_2 (10 mL) was added (–)-**3d** (512 mg, 1.6 mmol) at –40 °C. The mixture was stirred at –40 °C for 12 h, after which time it was treated with saturated aq. $NaHCO_3$ (2 × 5 mL), the two phases were separated and the organic layer was washed with brine (2 mL), dried over $MgSO_4$, filtered and evaporated. The residue was purified by column chromatography (cyclohexane/EtOAc, 2:1 to 1:1) to furnish **29**[10] (75 mg, 49%) as a colorless oil. IR (neat) ν_{max} 3439, 2918, 2850, 1716, 1042 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.53 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 2.70 (s, 3H), 2,41 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 142.6 (Cq), 141.7 (Cq), 130.3 (CH), 123.8 (CH), 44.2 (CH$_3$), 21.6 (CH$_3$); EIMS *m/z* (rel. intensity) 154 (M$^+$, 6), 139 (15), 91 (12), 63 (18), 18 (100); HPLC analysis (column Chiralcel AS-H, *n*-hexane/*iso*-propanol, 50:50, 0.5 mL/min, λ_{max} = 243 nm): Rt(*R*) = 19.3 min and Rt(*S*) = 26.2 min, %Rt(*R*) / %Rt(*S*) = 54/46.

Under the same conditions, **28** (42 mg, 0.3 mmol) in CH_2Cl_2 (3 mL) was converted using (+)-**3d** (155 mg, 0.5 mmol) into **29** (31 mg, 67%) as a 46.7:53.3 (7% ee) mixture of the (*R*)- and (*S*)-enantiomers.

[10] Tohma, H.; Takizawa, S.; Watanabe, H.; Fukuoka, Y.; Maegawa, T.; Kita, Y. *J. Org. Chem.* **1999**, *64*, 3519–3523.



using (R)-(–)-**4a** (R = Me): 100%, ee = 20 %
using **4d₁** (R = i-Pr): 71%, ee = 9%
using **4d₂** (R = i-Pr): 75%, ee = 7%

3,10-Dihydroxy-3,5,8,10-tetramethyltricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione (6a). To a stirred solution of 2,6-dimethylphenol (**5a**, 10 mg, 0.08 mmol) in THF (1.2 mL) at –78 °C was added *(R)*-**4a** (28 mg, 1.1 equiv). The mixture was stirred at –78 °C until complete conversion of **5a** was observed by TLC (petroleum ether/acetone, 3:1). One drop of TFA was then added and the reaction mixture was further stirred at rt for 1 h, after which time it was diluted with EtOAc (10 mL), washed with saturated aq. $NaHCO_3$ (3 × 5 mL) and brine (5 mL), dried over Na_2SO_4, filtered and evaporated. The resulting residue was purified by column chromatography (CH_2Cl_2/MeOH, 40:1) to furnish **6a**[11] (13 mg, quant.) as a slightly yellow solid: mp = 180 °C (lit.[12] mp = 194-196 °C); IR (neat) ν_{max} 3419, 1713, 1671 cm^{-1}; NMR ^{1}H ($CDCl_3$, 300 MHz) δ 6.23-6.30 (m, 2H), 5.51 (d, J = 8.3 Hz, 1H), 4.00 (brs, 2H), 3.39 (d, J = 6.8 Hz, 1H), 3.25 (dd, J = 1.9, 8.3 Hz , 1H), 2.84-2.89 (m, 1H), 1.85 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H), 1.24 (s, 3H); NMR ^{13}C ($CDCl_3$, 100 MHz) δ 214.8 (C=O), 203.0 (C=O), 139.2, 135.8, 135.3, 133.3, 73.6, 73.0, 53.8, 44.2, 43.7, 42.8, 31.7 (CH_3), 26.2 (CH_3), 16.3 (CH_3), 15.6 (CH_3); EIMS m/z (rel. intensity): 276 (M$^+$, 5), 242 (3), 138 (42), 122 (15), 121 (33), 43 (100); HPLC analysis (column Chiralcel AS-H, *n*-hexane/*iso*-propanol, 50:50, 0.5 mL/min, λ_{max} = 225 nm): Rt = 9.3 and 13.2 min, %Rt1 / %Rt2 = 40.2/59.8 (20% ee).

To a stirred solution of **5a** (30 mg, 0.25 mmol) in THF (3.6 mL) at –40 °C was added (–)-**4d₁** (93 mg, 0.27 mmol). The mixture was stirred at –40 °C for 12 h, after which time one drop of TFA was added. This mixture was further stirred at rt for 1 h and filtered. The remaining solid was washed with CH_2Cl_2 (2 × 2 mL) and the combined filtrates were evaporated to give a residue, which was purified by column chromatography (petroleum ether/acetone, 5:1) to furnish **6a** (24.5 mg, 71%) as a slightly yellow solid. HPLC analysis (column Chiracel AS-H,

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[11] Lebrasseur, N.; Gagnepain, J.; Ozanne-Beaudenon, A.; Léger, J.-M.; Quideau, S. *J. Org. Chem.*, **2007**, *72*, 6280–6283.
[12] Adler, E.; Dahlen, J. ; Westin, G. *Acta Chem. Scand.* **1960**, *14*, 1580–1596.

n-hexane/*iso*-propanol, 50:50, 0.5 mL/min, λ_{max} = 225 nm): Rt = 9.3 and 13.3 min, %Rt1 / %Rt2 = 54.6/45.4 (9% ee).

To a stirred solution of **5a** (31 mg, 0.25 mmol) in THF (3.6 mL) at –40 °C was added (–)-**4d$_2$** (93 mg, 0.27 mmol). The mixture was stirred at –40 °C for 12 h, after which time one drop of TFA was added. This mixture was further stirred at rt for 1 h and filtered. The remaining solid was washed with CH_2Cl_2 (2 × 2 mL) and the combined filtrates were evaporated to give a residue, which was purified by column chromatography (petroleum ether/acetone, 5:1) to furnish **6a** (26 mg, 75%) as a slightly yellow solid. HPLC analysis (column Chiracel AS-H, *n*-hexane/*iso*-propanol, 50:50, 0.5 mL/min, λ_{max} = 225 nm): Rt = 9.4 and 13.2 min, %Rt1 / %Rt2 = 46.5/53.5 (7% ee).

Preliminary Evaluation of Reaction Conditions for In Situ Generation of HPD-Mediating Iodanes from Iodoarenes

General Procedure A. To a stirred solution of partially dried (overnight under high vacuum) and titrated[13] *m*-CPBA (*ca*. 70% w/w, 1 equiv) in dry CH_2Cl_2 (⇒ [arenol] = 0.33 M) was added the iodoarene. After stirring at rt for 1 h, the starting arenol (1 equiv) was added under N_2. The mixture was stirred for 2-3 h until no more evolution of the reaction progress was observed by TLC monitoring (petroleum ether/acetone, 3:1), and it was then cooled down to –90 °C. The resulting precipitate was filtered, washed twice with cold CH_2Cl_2 (–90 °C, 2 × 1 mL per mmol of starting arenol used) and the filtrates were combined and evaporated to give a residue, which was purified by column chromatography.

2,6-Dimethylphenol (**5a**, 1.22 g, 10 mmol) was submitted to the general procedure A for 2 h using 2-iodophenylacetic acid (**1f**, 262 mg, 1 mmol, 0.1 equiv) to afford, after purification by column chromatography (cyclohexane/EtOAc, from 7:1 to 3:2), recovered **5a** (192 mg, 16%), **6a** (759 mg, 55 %) as a slightly yellow solid and the epoxyde **7a** (123 mg, 8%) as a yellow oil. **7a**: IR (neat) ν_{max} 3498, 1685, 1654, 1238, 1172, 1107, 1011 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.86 (d, J = 7.6 Hz, 1H), 3.72 (br s, 1H), 3.66 (d, J = 4.0 Hz, 1H), 3.54 (d, J = 4.0 Hz,

[13] Oxidation of an excess of *p*-tolylsulfide by dried *m*-CPBA in CH_2Cl_2 at rt for 1 h ([sulfide] = 0.1 M) gave a mixture of the starting material ant the corresponding sulfoxide. The relative integration of the ^1H NMR peaks of each components of the resulting mixture gave a titration of the *m*-CPBA.

1H), 1.88 (d, J = 4.0 Hz, 3H), 1.32 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.4 (C=O), 139.1 (CH $_{aro}$), 138.1 ($C_{q\ aro}$), 75.0 (*C*(O)CH_3), 56.0 (CH(O)), 47.6 (CH(O)), 24,6 (CH_3), 15.8 (CH_3); CIMS *m*/*z* (rel. intensity) 172 ($M+NH_4^+$, 100), 156 (11); HRMS (ESI) calcd for $C_8H_{10}O_3Na$ ($[M+Na]^+$) 177.0528, found 177.0533.

2,6-Dimethylphenol (**5a**, 609 mg, 5 mmol) was submitted to the general procedure A for 2 h using **1f** (1.30 g, 10 mmol, 1 equiv) to afford, after purification by column chromatography (cyclohexane/EtOAc, from 7:1 to 3:2), recovered **5a** (109 mg, 18 %), **6a** (401 mg, 58 %) and the epoxyde **7a** (46 mg, 3%).

2,6-Dimethylphenol (**5a**, 1.22 g, 10 mmol) was submitted to the general procedure A for 2 h using **1f** (5.24 g, 20 mmol, 2 equiv) to afford, after purification by column chromatography (cyclohexane/EtOAc, from 7:1 to 3:2), recovered **5a** (159 mg, 13 %) and **6a** (883 mg, 64 %).

To a stirred solution of partially dried and titrated *m*-CPBA (8.2 g, 33.3 mmol, 10 equiv) in acetone (67 mL) was added **1f** (86.5 mg, 0.33 mmol, 0.1 equiv) and 2,6-dimethylphenol **5a** (407 mg, 3.33 mmol, 1 equiv). This mixture was stirred at rt for 2 h, after which time it was evaporated to give a residue, which was triturated with cold CH_2Cl_2 (–90 °C) (10 mL). The resulting precipitate was filtered, washed with cold CH_2Cl_2 (2 × 3 mL) and the filtrates were combined, and evaporated. The resulting crude product was purified by column chromatography (cyclohexane/EtOAc, from 7:1 to 3:2) to furnish the epoxyde **7a** (241 mg, 47 %) as a yellow oil and the *para*-quinone 2,6-dimethylcyclohexa-2,5-diene-1,4-dione **32**[14] (41 mg, 9%) as a brown oil. **32**: IR (neat) ν_{max}: 2850, 1652, 1618, 1375, 1310, 1205, 1038; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.53 (s, 2H), 2.53 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 188.2 (CO), 187.6 (CO), 145.7 (Cq_{aro}), 133.2 (CH_{aro}), 15.9 (CH_3); CIMS *m*/*z* (rel. intensity) 154 ($M+NH_4^+$, 100).

[14] Liotta, D.; Arbiser, J.; Short, J. W.; Saindane, M. *J. Org. Chem.* **1983**, *48*, 2932-2933.

Iodoarene-Mediated Oxygenating Dearomatization of Select Arenols Using m-CPBA as Co-Oxidant

Iodoarene-Mediated Oxygenating Dearomatization of 2,4,6-trimethylphenol 5b

2,4,6-Trimethylphenol (**5b**, 1.36 g, 10 mmol) was submitted to the general procedure A for 3 h using **1f** (262 mg, 1 mmol) to afford, after purification by column chromatography (cyclohexane/EtOAc, from 7:1 to 3:2), recovered **5b** (286 mg, 21 %) as a white solid, 3,10-dihydroxy-3,5,7,8,10,11-hexamethyltricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione **6b**[11] (236 mg, 16%) as a white solid and the epoxyde **7b** (118 mg, 7%) as a slightly yellow oil. **6b**: mp = 179 °C (lit.[15] mp = 182-183 °C); IR (neat) ν_{max} 3483, 2987, 2862, 1669 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.03 (s, 1H), 5.04 (s, 1H), 3.92 (s, 1H), 3.15 (s, 1H), 2.79-2.81 (m, 1H), 2.21 (brs, 1H), 1.83 (d, J = 1.5 Hz, 3H), 1.70 (d, J = 1.5 Hz, 3H), 1.36 (s, 3H), 1.24 (s, 6H), 1.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 214.1, 202.4, 145.2, 145.1, 133.1; 127.6, 73.7, 72.2, 57.3, 48.7, 48.6, 32.4, 25.2, 23.2, 21.4, 16.2, 12.4; EIMS (EI) m/z (rel. intensity) 304 (M$^+$, 5), 152 (24), 110 (100). **7b**: IR (neat) 3488, 2961, 1682, 1370, 1175, 1142 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.67 (s, 1H), 3.65 (s, 1H), 3.48 (s, 1H), 1.85 (s, 3H), 2.79-2.81 (m, 1H), 1.56 (s, 3H), 1.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.4, 144.0, 136.2, 74.8, 62.5, 54.4, 24.8, 20.6, 15.6; CIMS m/z (rel. intensity): 186 (M+NH_4^+, 100); HRMS (ESI) calcd for $C_9H_{12}O_3Na$ ([M+Na]$^+$) 191.0684, found 191.0677.

2,4,6-Trimethylphenol (**5b**, 136 mg, 1 mmol) was submitted to the general procedure A for 2 h using **1f** (524 mg, 2 mmol) to afford, after purification by column chromatography (cyclohexane/EtOAc, from 7:1 to 3:2), recovered **5b** (14 mg, 10 %), the dimer **7b** (41 mg, 27%) as a white solid, and the *m*-chlorobenzoyl ester **7b'** (32 mg, 11%) as a yellow oil. **7b'**: IR (neat) ν_{max} 3063, 3021, 1717, 1652, 1621, 1386, 1210 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.01 (s, 1H), 7.90 (d, J = 7.7 Hz, 1H), 7.54-7.51 (m, 1H), 7.36 (t, J = 7.7 Hz, 1H), 6.72 (s, 1H), 5.87 (s, 1H), 1.97 (s, 3H), 1.94 (s, 3H), 1.51 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.4, 163.8, 141.9, 134.4, 133.5, 133.3, 133.2, 131.1, 130.4, 130.0, 129.6, 128.0, 79.1, 24.2, 21.2, 15.3; EIMS m/z (rel. intensity): 292 (M+H$^+$, 100), 291 (34), 290 (15), 255 (11), 152 (21); HRMS (ESI) calcd for $C_{16}H_{15}ClNaO_3$ ([M+Na]$^+$) 313.0607, found 313.0615.

[15] Adler, E.; Holmberg, K.; Ryrfors, L.-O. *Acta Chem. Scand.* **1974**, B*28*, 465–472.

Iodoarene-Mediated Oxygenating Dearomatization of Carvacrol 5c

Carvacrol (**5c**, 1.50 g, 10 mmol) was submitted to the general procedure A for 3 h using **1f** (262 mg, 0.1 mmol) to afford, after purification by column chromatography (cyclohexane/EtOAc, from 7:1 to 3:2), recovered carvacrol **5c** (510 mg, 34 %) as a slightly brown liquid, *rac*-biscarvacrol **6c**[11] (315 mg, 19 %) as a white solid, the epoxyde **7c** (110 mg, 6%) as a yellow oil and the *para*-quinone 2-*iso*-propyl-5-methylcyclohexa-2,5-diene-1,4-dione **7c'**[16] (377 mg, 23 %) as a yellow oil. **6c**: mp = 137 °C (lit.[17] mp =138-139 °C); IR (neat) ν_{max} 3451, 2967, 1724, 1676, 1157 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 5.97 (s, 1H), 5.86 (d, J = 7.0 Hz, 1H), 4.04 (bs, 2H), 3.37 (dd, J = 2.3, 6.8 Hz, 1H), 3.23 (dd, J = 1.5, 8.9 Hz , 1H), 3.15-3.17 (m, 1H), 3.12 (dd, J = 2.3, 8.7 Hz , 1H), 2.53-2.45 (m, 1H), 1.89-1.81 (m, 1H), 1.26 (s, 3H), 1.24 (s,3H), 1.15 (d, J = 4.1 Hz, 3H), 1.13 (d, J = 4.3 Hz, 3H), 0.91 (d, J = 6.8 Hz, 3H), 0.86 (d, J = 7.0 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 212.3, 201.9, 166.5, 145.7, 126.1, 120.0, 73.5, 73.0, 55.8, 44.6, 42.1, 41.0, 33.3, 32.9, 32.3, 25.9, 23.0, 20.8, 20.1, 19.3; EIMS *m*/*z* (rel. intensity) 332 (M $^+$, 32), 315 (16), 289 (14), 271 (34), 243 (40), 166 (26), 149 (39), 125 (100). **7c**: IR (neat) ν_{max} 3510, 1688, 1661, 1381, 1238, 1180, 1130 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 5.93 (s, 1H), 3.69 (d, J = 4.0 Hz, 1H), 3.65 (brs, 1H), 3.51 (m, 1H), 2.68 (m, 1H), 1.34 (s, 3H), 1.24 (d, J = 7.2 Hz, 3H), 1.21 (d, J = 7.0 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 198.7, 167.1, 121.1, 74.2, 56.4, 50.5, 34.6, 24.9, 20.5, 20.1; CIMS *m*/*z* (rel. intensity) 200 (M+NH$_4^+$, 100); HRMS (ESI) calcd for $C_{10}H_{14}O_3Na$ ([M+Na]$^+$) 205.0844, found: 205.084 4. **7c'**:[16] IR (neat) ν_{max} 1672, 1648, 1381, 1276 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 6.57 (s, 1H), 6.51 (s, 1H), 3.06-2.96 (m,1H), 2.03 (s, 3H), 1.13 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 188.6, 187.4, 154.9, 145.2, 133.8, 130.3, 26.5, 21.4, 15.3; CIMS *m*/*z* (rel. intensity) 182 (M+NH$_4^+$, 51), 18 (100).

The same reaction performed using 1.5 equiv of *m*-CPBA gave *rac*-biscarvacrol **6c** (531 mg, 32 %), the epoxyde **7c** (183 mg, 10 %) as a yellow oil and **7c'** (606 mg, 37%) as a yellow oil.

Carvacrol (**5c**, 150 mg, 1 mmol) was submitted to the general procedure A for 2.5 h using **1f** (524 mg, 2 mmol) to afford, after purification by column chromatography (cyclohexane/EtOAc, from 7:1 to 3:2), carvacrol **5c** (24 mg, 16 %) as a slightly brown liquid and *rac*-biscarvacrol **6c** (68 mg, 41%) as a white solid.

[16] Takizawa, Y.; Munakata, T.; Iwasa, Y.; Suzuki, T.; Mitsuhashi, T. *J. Org. Chem.* **1985**, *50*, 4383–4386.
[17] Carman, R. M.; Lambert, L. K. ; Robinson, W. T. ; Van Dongen, J. M. A. M. *Aust. J. Chem.* **1986**, *39*, 1843–1850.

Iodoarene-Mediated Oxygenating Dearomatization of 2-Methylnaphthol 5d

2-Methylnaphthol (**5d**, 158 mg, 1 mmol) was submitted to the general procedure A for 2 h using **1f** (27 mg, 0.1 mmol) to afford, after purification by column chromatography (petroleum ether/acetone 4:1), recovered **5d** (55 mg, 34%) as a slightly pink solid, the *ortho*-quinol **6d** (23 mg, 13%) as a reddish oil and the epoxyde **7d** (70 mg, 37%) as a yellow oil. **6d**: IR (neat) ν_{max} 3452, 2873, 1692, 1293 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.98 (d, J = 7.5 Hz, 1H), 7.59 (td, J =1.1, 7.5 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 6.48 (d, J = 9.8 Hz, 1H), 6.32 (d, J = 9.8 Hz, 1H), 2.46 (brs, 1H), 1.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 204.2 (C=O), 137.8 ($C_{q\ aro}$), 137.0 ($CH_{\ aro}$), 135.2 ($C_{q\ aro}$), 128.2 ($CH_{\ aro}$), 128.1 ($CH_{\ aro}$), 127.5 ($CH_{\ aro}$), 127.2 ($CH_{\ aro}$), 124.2 ($CH_{\ aro}$), 75.3 (*C*(O)CH_3), 28.5 (CH_3). EIMS *m*/*z* (rel. intensity) 174 (M^+, 9), 131 (17), 28 (100). **7d**: IR (neat) ν_{max} 3452, 2873, 1702, 1611, 1384, 1293, 1107 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.89 (d, J = 7.6 Hz, 1H), 7.64-7.58 (m, 2H), 7.53-7.46 (m, 2H), 4.11 (d, J = 4.2 Hz, 1H), 3.93 (brs, 1H), 3.88 (d, J = 4.2 Hz, 1H), 1.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.9, 138.5, 133.9, 130.2, 129.7, 129.6, 128.3, 75.2, 57.0, 52.9, 24.2; CIMS *m*/*z* (rel. intensity) 208 ($M+NH_4^+$, 100), 192 (42), 166 (22); HRMS (ESI) calcd for $C_{11}H_{10}O_3Na$ ($[M+Na]^+$) 213.0528, found: 213.0518.

2-Methylnaphthol (**5d**, 158 mg, 1 mmol) was submitted to the general procedure A for 2 h using **1f** (262 mg, 1 mmol) to afford, after purification by column chromatography (petroleum ether/acetone 4:1), recovered **5d** (39 mg, 25 %) as a slightly pink solid and the *ortho*-quinol **6d** (116 mg, 67%) as a reddish oil.

2-Methylnaphthol (**5d**, 158 mg, 1 mmol) was submitted to the general procedure A for 2.5 h using **1f** (525 mg, 2 mmol) to afford solely, after purification by column chromatography (petroleum ether/acetone, 4:1), the *ortho*-quinol **6d** (143 mg, 82 %) as a redish oil.

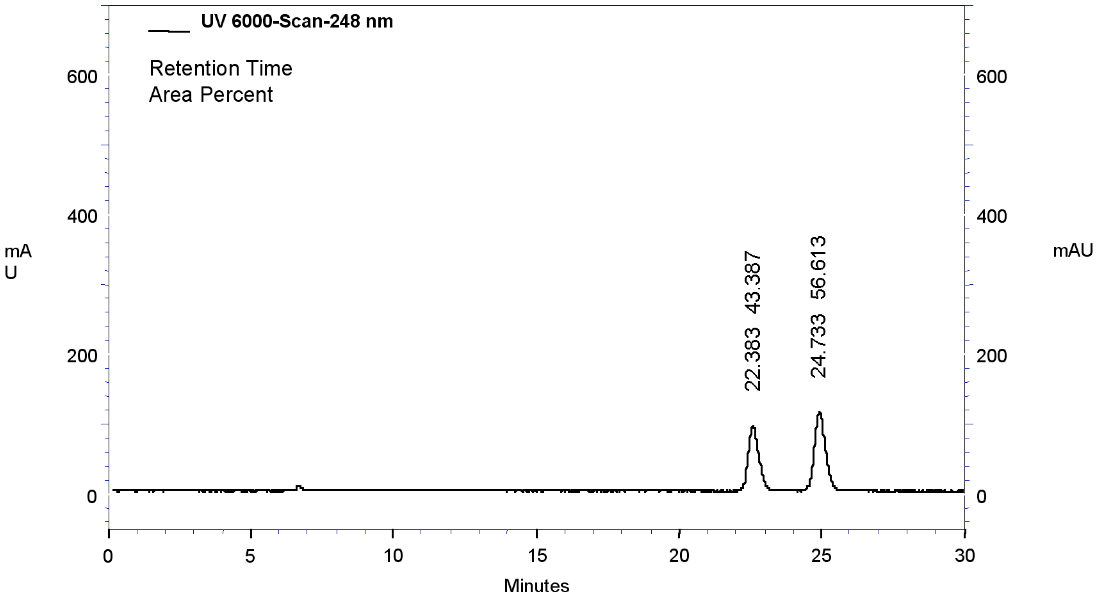
To a stirred solution of partially dried and titrated *m*-CPBA (*ca*. 70% w/w, 620 mg, 2.5 mmol) in dry CH_2Cl_2 (3 mL) was added **1f** (26 mg, 0.1 mmol) and, after 1 h, 2-methylnaphthol (**5d**, 158 mg, 1 mmol). This mixture was stirred for 3 h and then cooled down to –90 °C. The resulting precipitate was filtered, washed with cold CH_2Cl_2 (2 × 1 mL) and the filtrates were combined, and evaporated to give a residue, which was purified by column chromatography (petroleum ether/acetone, 4:1) to furnish solely the epoxyde **7d** (173 mg, 91 %).

Enantioselective Iodoarene-Mediated Oxygenating Dearomatization of 2-Methylnaphthol Using m-CPBA as Co-Oxidant

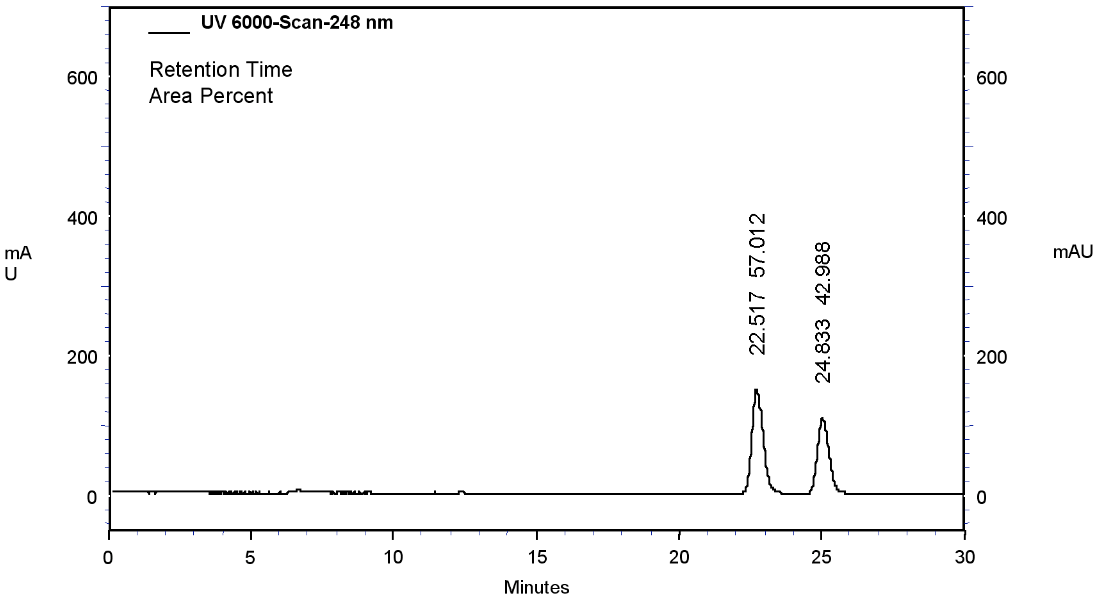
General Procedure A'. This procedure is identical to the general procedure A using 1 equiv of *m*-CPBA, but 2-methylnaphthol (**5d**, 1 equiv) is in each case used as the starting arenol together with a different chiral iodoarene (ArI*, 1 equiv) in place of 2-iodophenyl acetic acid **1f**. After purification by column chromatography (petroleum ether/acetone 7:1), the *ortho*-quinol **6d** was obtained. Its analytical chiral HPLC separation was performed using a Chiralcel AS-H column, eluting with *n*-hexane/*iso*-propanol (80:20) at a flow rate of 0.5 mL/min, and a detection at a λ_{max} of 231 nm): Rt = 11.3-11.6 min and 14.0-14.2 min.

General Procedure B. To a stirred solution of partially dried *m*-CPBA (2.5 equiv) in anhydrous CH_2Cl_2 (⇒ [arenol] = 0.33 M) was added ArI* (0.1 equiv) and, after 1 h, the starting naphthol **5d** (1 equiv). The mixture was stirred for 2-3 h and then cooled down to –90 °C. The resulting precipitate was filtered, washed with cold CH_2Cl_2 (–90 °C, 2 × 1 mL per mmol of arenol) and the filtrates were combined and evaporated to give a residue, which was purified by column chromatography (petroleum ether/acetone, 4:1) to furnish solely the epoxyde **7d**. Its analytical chiral HPLC separation was performed using a Chiralcel AS-H column, eluting with *n*-hexane/*iso*-propanol (80:20) at a flow rate of 0.5 mL/min, and a detection at a λ_{max} of 248 nm): Rt = 22.4-23.1 and 24.8-25.4 min.

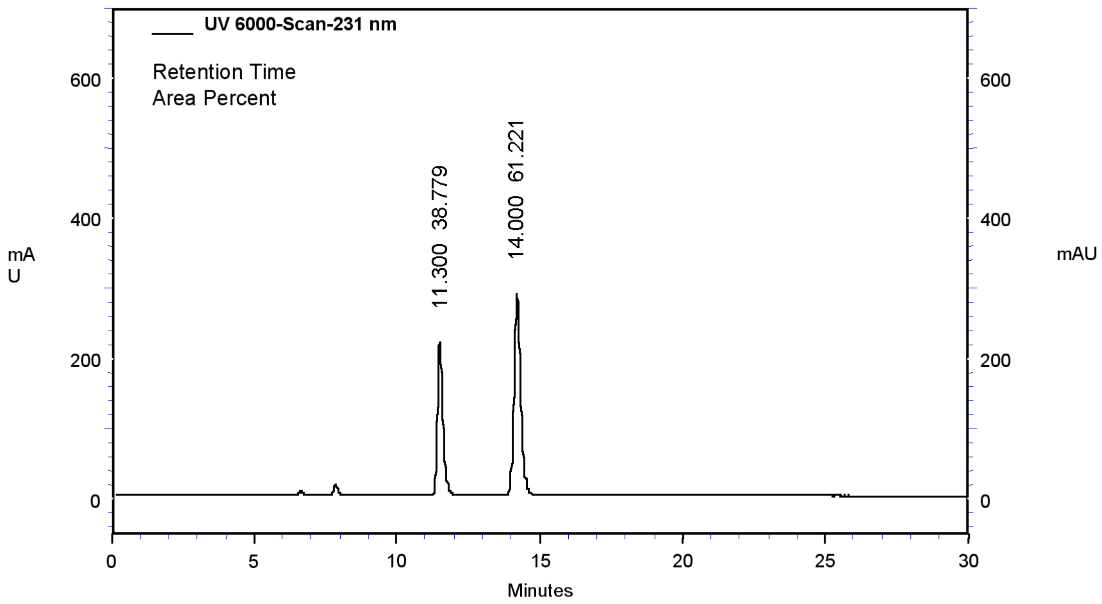
2-Methylnaphthol (**5d**, 79 mg, 0.5 mmol) was submitted to the general procedure B for 2.5 h using (–)-2-(2-iodophenyl)-3-methylbutanoic acid (–)-**1d** (15.2 mg, 0.05 mmol) to furnish the epoxide **7d** (80 mg, 84%) in 13% enantiomeric excess:



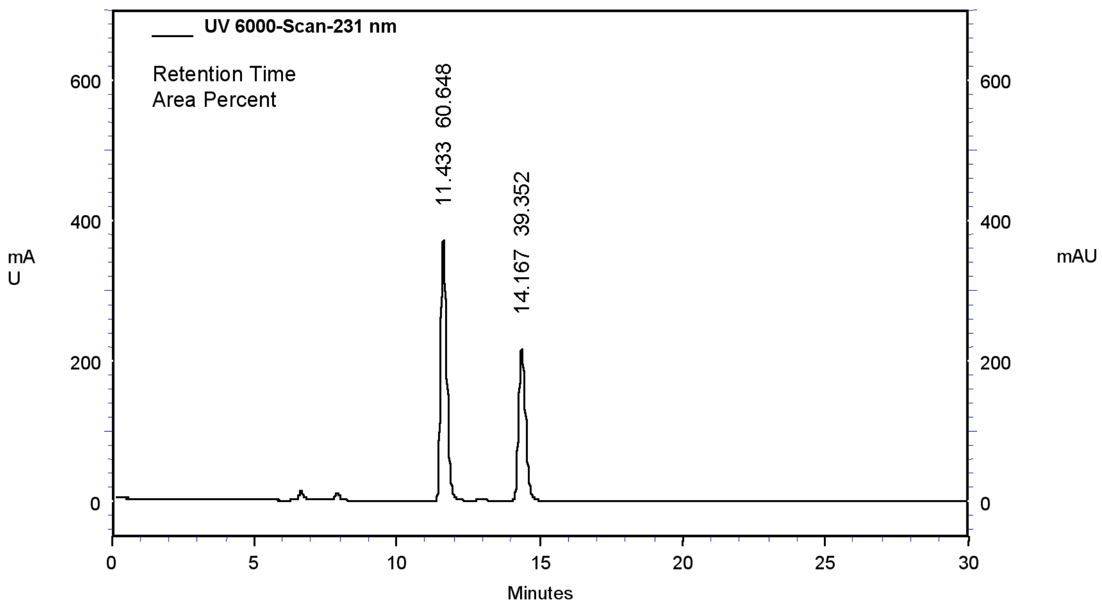
2-Methylnaphthol (**5d**, 79 mg, 0.5 mmol) was submitted to the general procedure B for 2.5 h using (+)-2-(2-iodophenyl)-3-methylbutanoic acid (+)-**1d** (15.3 mg, 0.05 mmol) to furnish the epoxide **7d** (84.7 mg, 89%) in 14% enantiomeric excess:



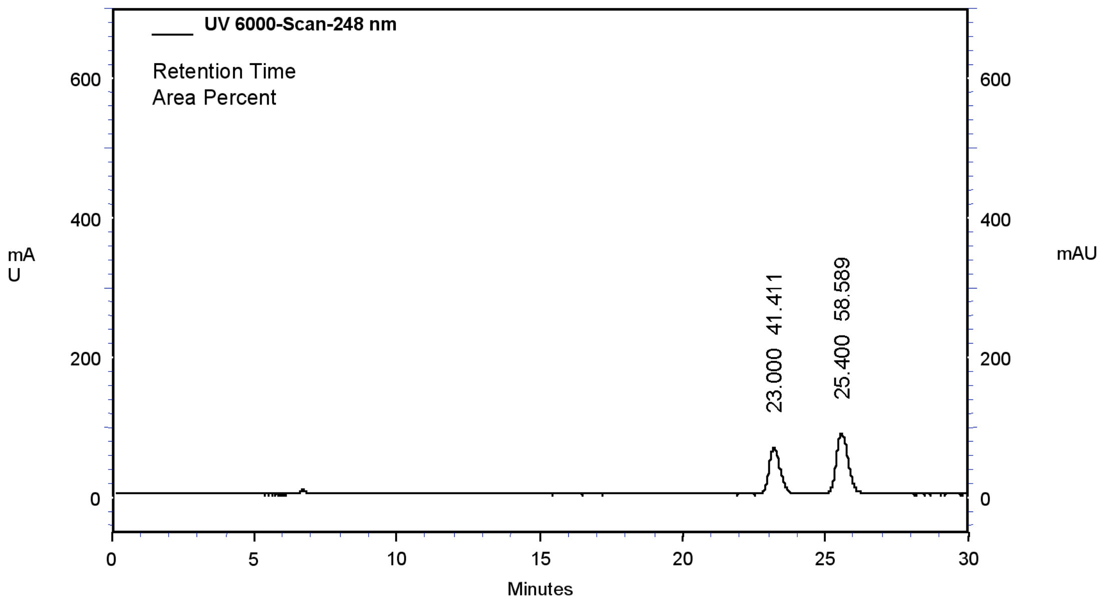
2-Methylnaphthol (**5d**, 79 mg, 0.5 mmol) was submitted to the general procedure A' for 2 h using (–)-**1d** (153 mg, 0.5 mmol) to furnish the *ortho*-quinol **6d** (64 mg, 73%) in 22% enantiomeric excess:



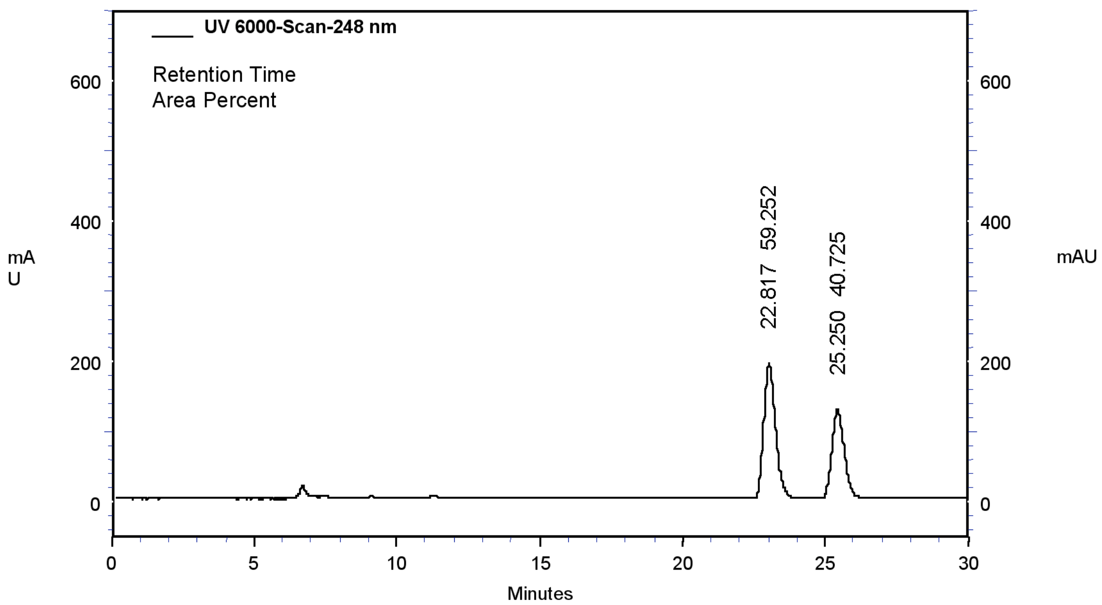
2-Methylnaphthol (**5d**, 306 mg, 2 mmol) was submitted to the general procedure A' for 3 h using (+)-**1d** (608 mg, 2 mmol) to furnish the *ortho*-quinol **6d** (244 mg, 70%) in 21% enantiomeric excess:



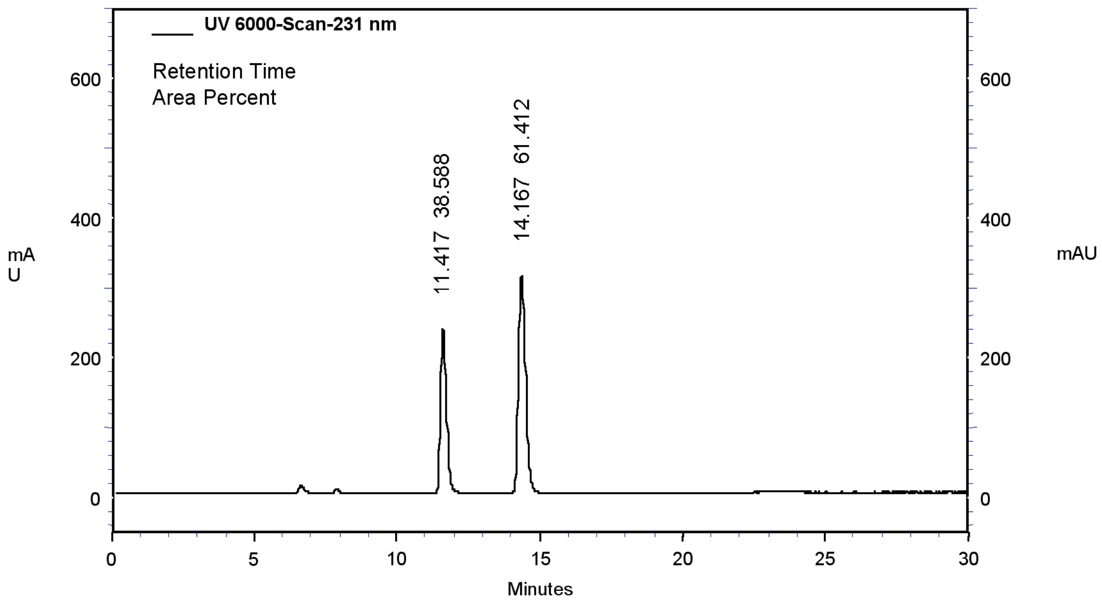
2-Methylnaphthol (**5d**, 40 mg, 0.25 mmol) was submitted to the general procedure B for 2.5 h using (–)-2-(2-iodophenyl)-4-methylpentanoic acid (–)-**1e** (8 mg, 0.025 mmol) to furnish the epoxide **7d** (43 mg, 91%) in 17% enantiomeric excess:



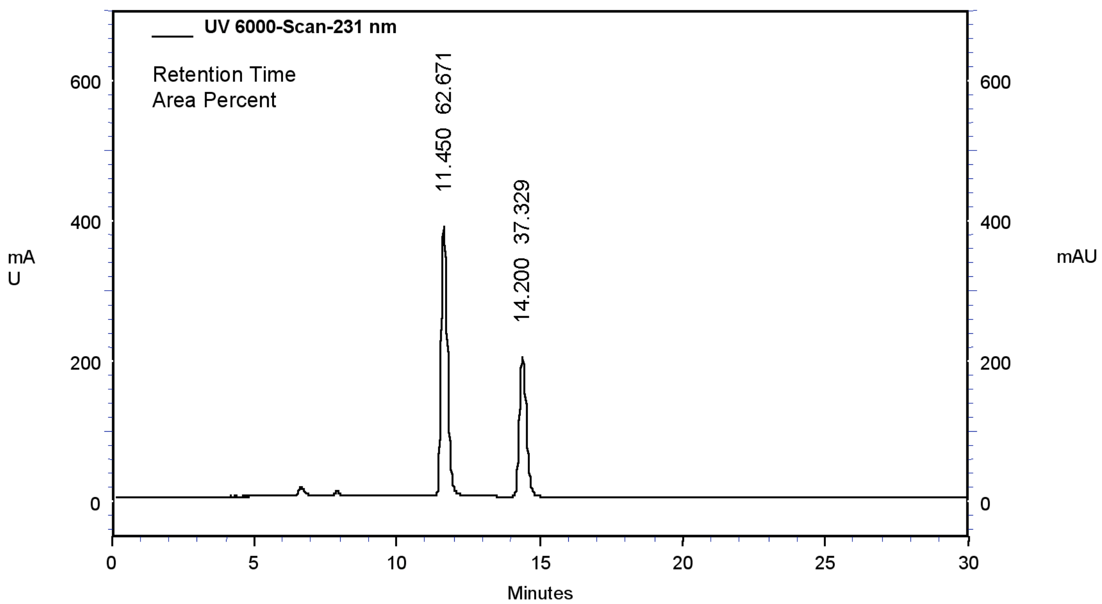
2-Methylnaphthol (**5d**, 63 mg, 0.4 mmol) was submitted to the general procedure B for 2 h using (+)-2-(2-iodophenyl)-4-methylpentanoic acid (+)-**1e** (12.8 mg, 0.04 mmol) to furnish the epoxide **7d** (66 mg, 87%) in 18% enantiomeric excess:



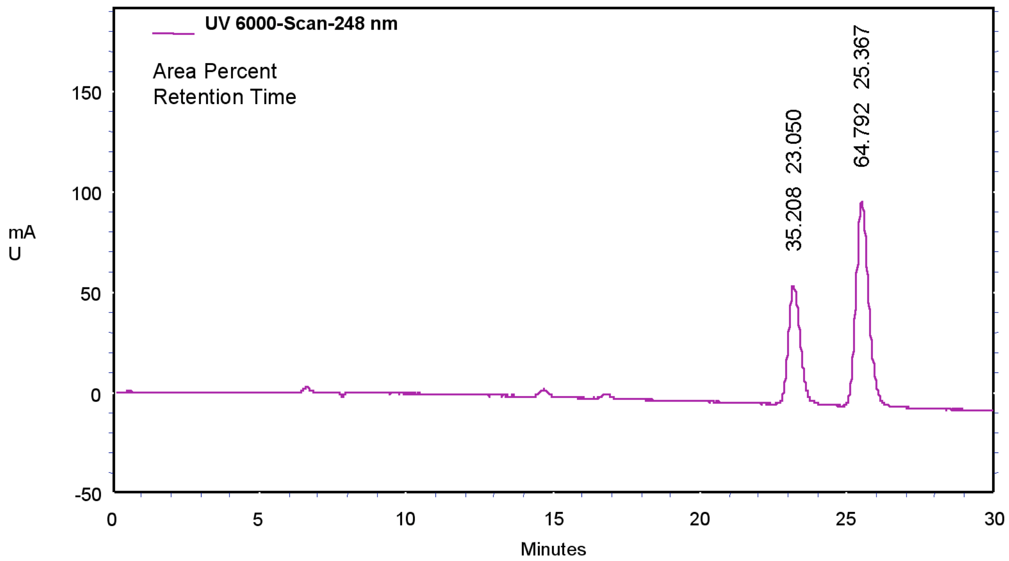
2-Methylnaphthol (**5d**, 158 mg, 1 mmol) was submitted to the general procedure A' for 3 h using (–)-**1e** (318 mg, 1 mmol) to furnish the *ortho*-quinol **6d** (125 mg, 72%) in 23% enantiomeric excess:



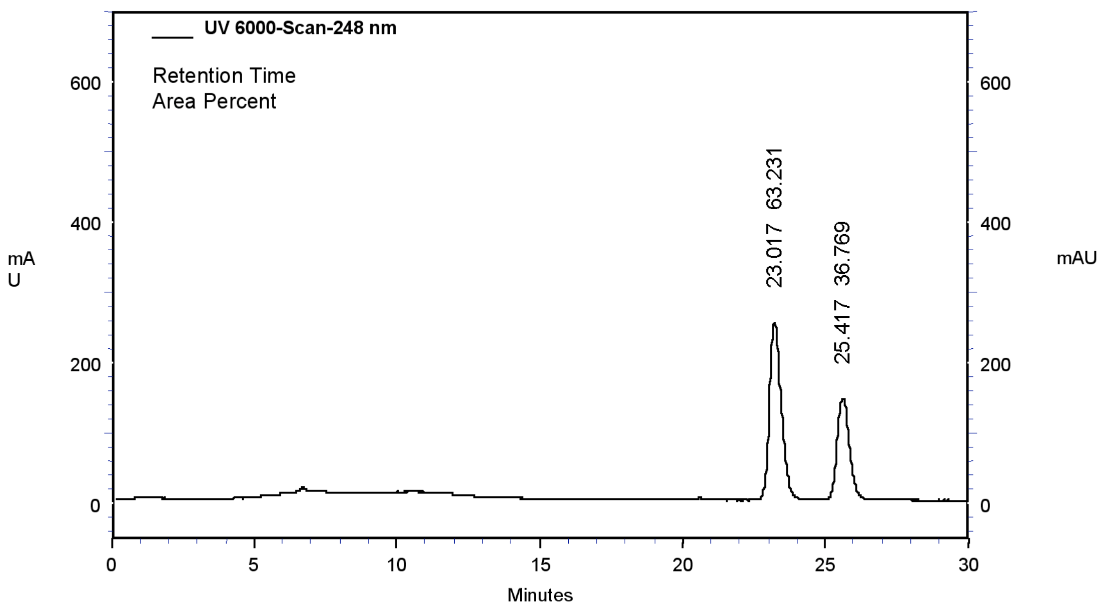
2-Methylnaphthol (**5d**, 79 mg, 0.5 mmol) was submitted to the general procedure A' for 3 h using (+)-**1e** (160 mg, 0.5 mmol) to furnish the *ortho*-quinol **6d** (60 mg, 69%) in 25% enantiomeric excess:



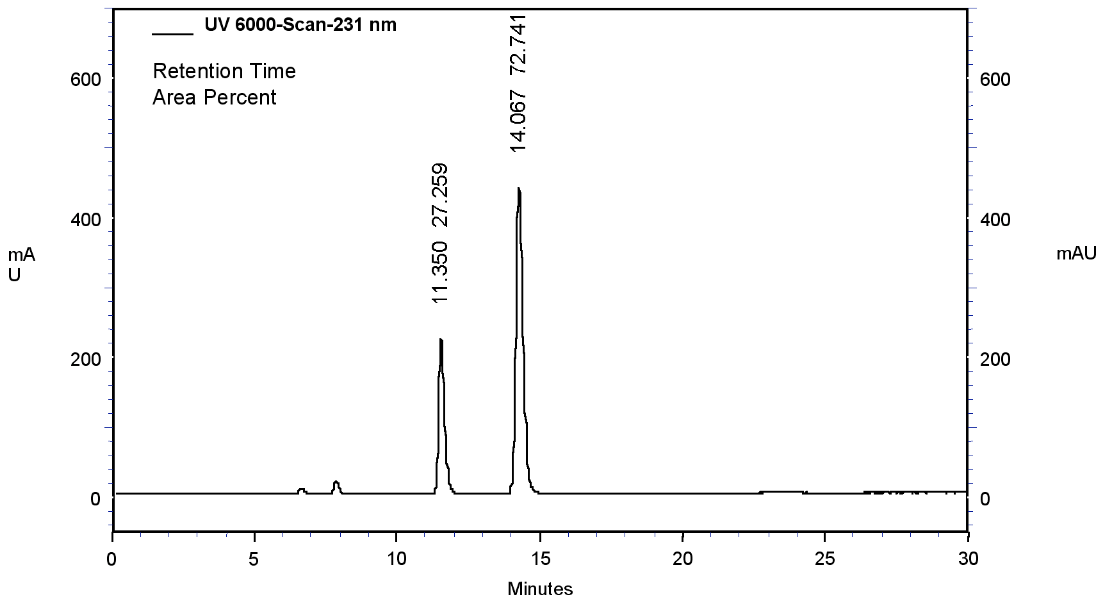
2-Methylnaphthol (**5d**, 79 mg, 0.5 mmol) was submitted to the general procedure B for 2 h using (–)-3-iodo-4-(2-methoxynaphthalen-1-yl)naphthalene-2-carboxylic acid (–)-**2b** (22.7 mg, 0.05 mmol) to furnish the epoxide **7d** (86 mg, 90%) in 29% enantiomeric excess:



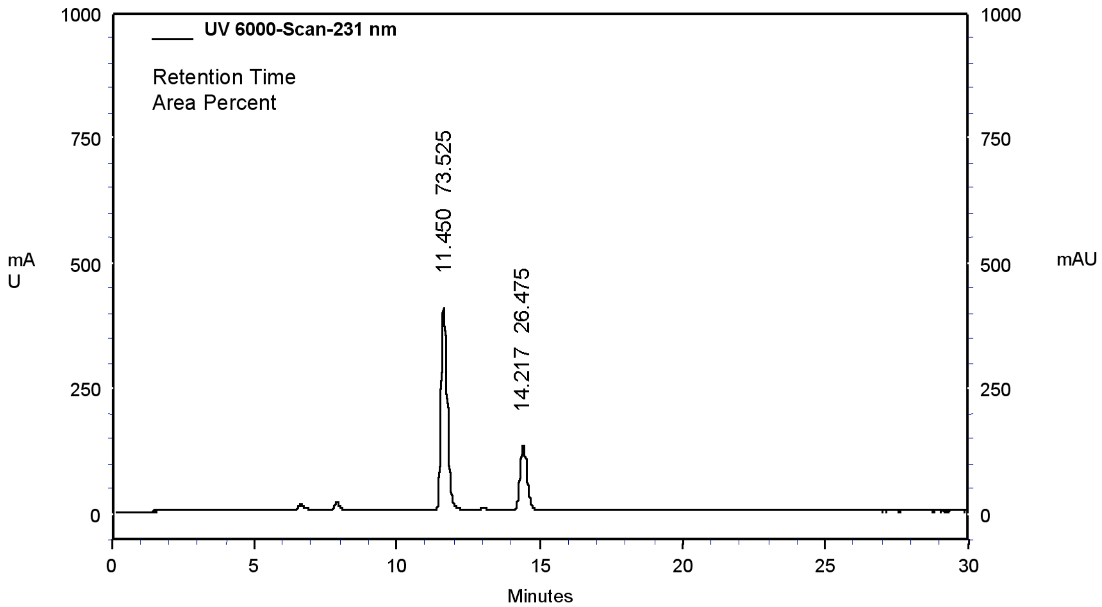
2-Methylnaphthol (**5d**, 78 mg, 0.5 mmol) was submitted to the general procedure B for 2 h using (+)-3-iodo-4-(2-methoxynaphthalen-1-yl)naphthalene-2-carboxylic acid (+)-**2b** (22.5 mg, 0.05 mmol) to furnish the epoxide **7d** (76 mg, 82%) in 26% enantiomeric excess:



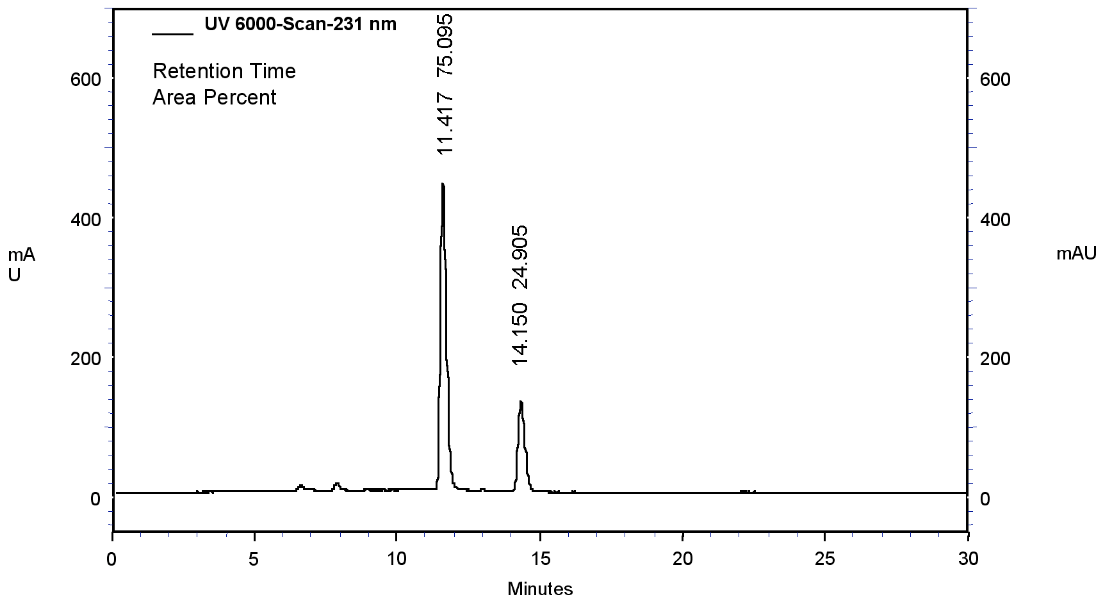
2-Methylnaphthol (**5d**, 15.8 mg, 0.1 mmol) was submitted to the general procedure A' for 3 h using (–)-**2b** (45.4 mg, 0.1 mmol) to furnish the *ortho*-quinol **6d** (11.6 mg, 67%) in 45% enantiomeric excess:



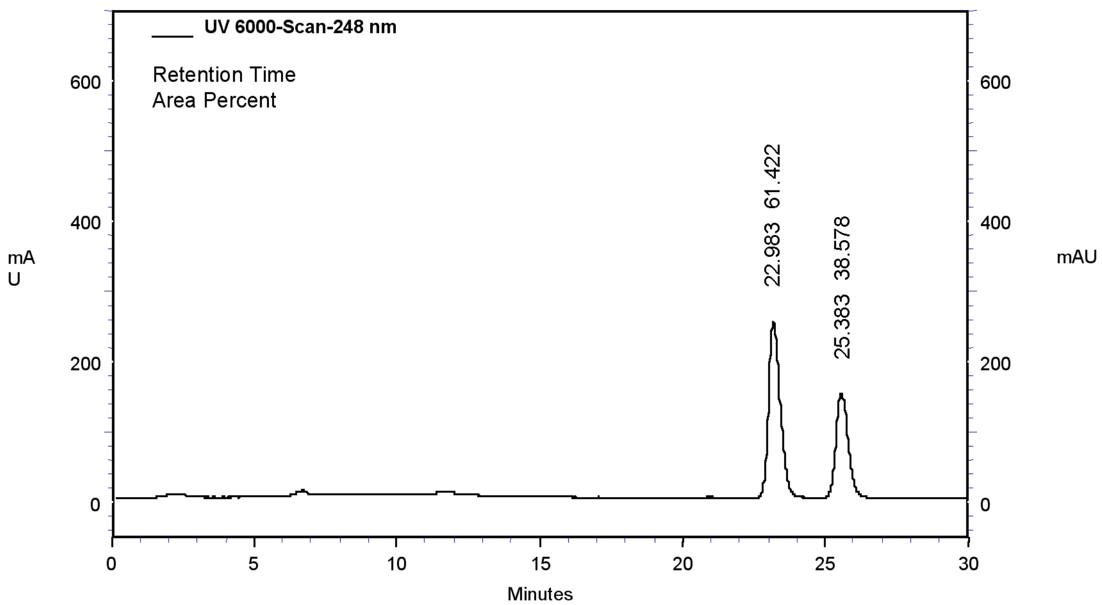
2-Methylnaphthol (**5d**, 15.8 mg, 0.1 mmol) was submitted to the general procedure A' for 3 h using (+)-**2b** (45.3 mg, 0.1 mmol) to furnish the *ortho*-quinol **6d** (13.5 mg, 71%) in 47% enantiomeric excess:



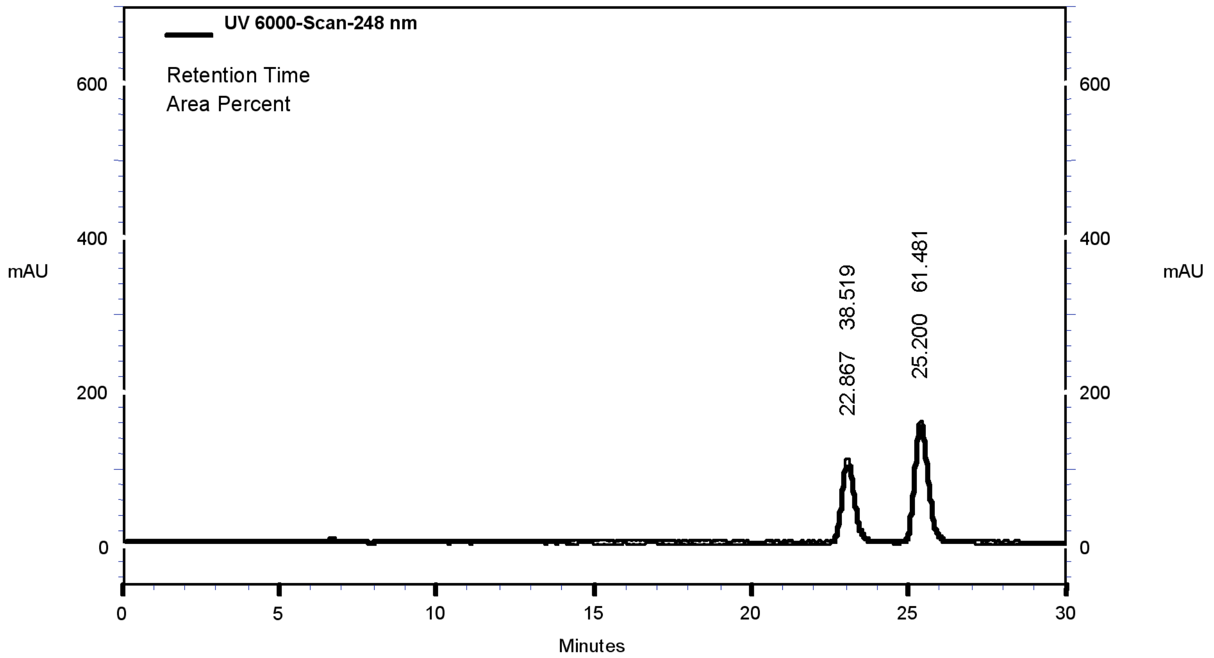
2-Methylnaphthol (**5d**, 15.9 mg, 0.1 mmol) was submitted to the general procedure A' for 3 h using (+)-**2b** (91 mg, 0.2 mmol) to furnish the *ortho*-quinol **6d** (14.5 mg, 83%) in 50% enantiomeric excess:



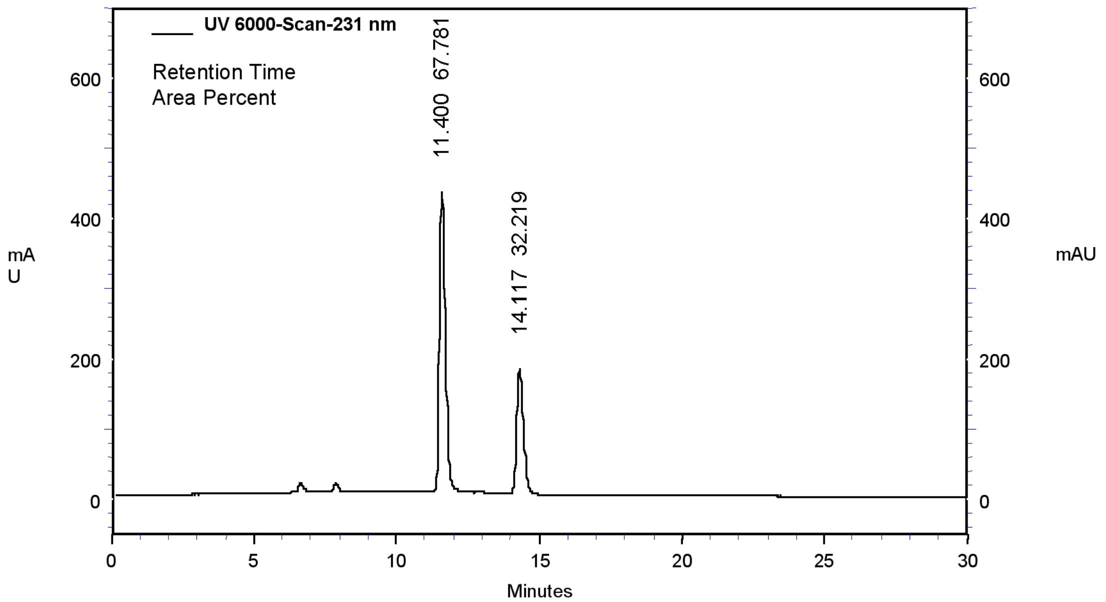
2-Methylnaphthol (**5d**, 79 mg, 0.5 mmol) was submitted to the general procedure B for 3 h using 3-(2-methoxyphenyl)-4,5-dimethoxy-2-iodobenzoic acid (–)-**2c** (21 mg, 0.05 mmol) to furnish the epoxide **7d** (75 mg, 79%) in 23% enantiomeric excess:



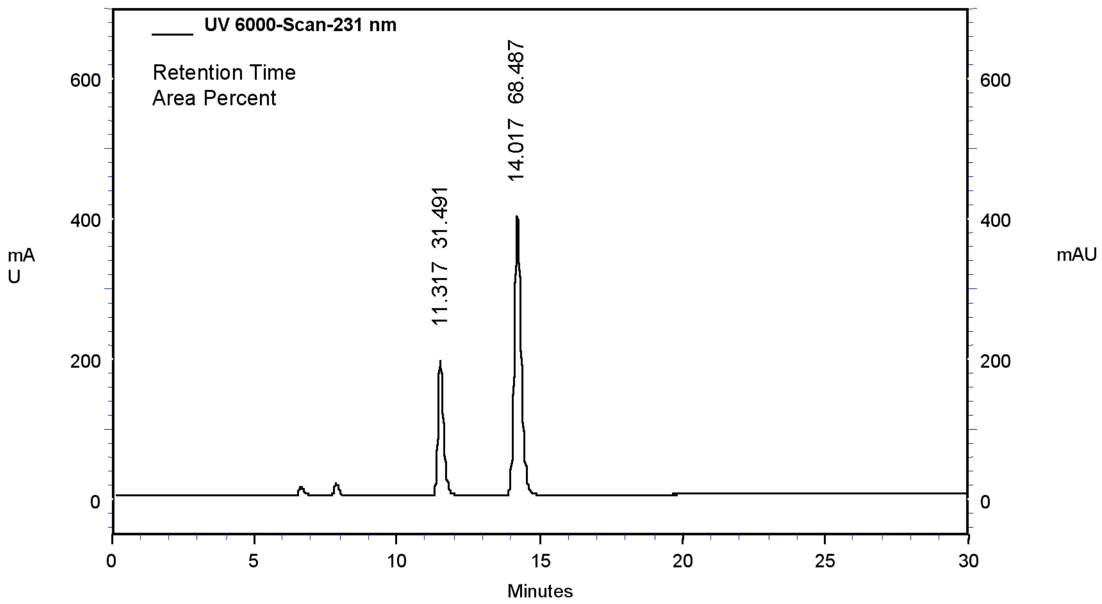
2-Methylnaphthol (**5d**, 39.5 mg, 0.5 mmol) was submitted to the general procedure B for 2.5 h using 3-(2-methoxyphenyl)-4,5-dimethoxy-2-iodobenzoic acid (+)-**2c** (21 mg, 0.05 mmol) to furnish the epoxide **7d** (43 mg, 90%) in 23% enantiomeric excess:



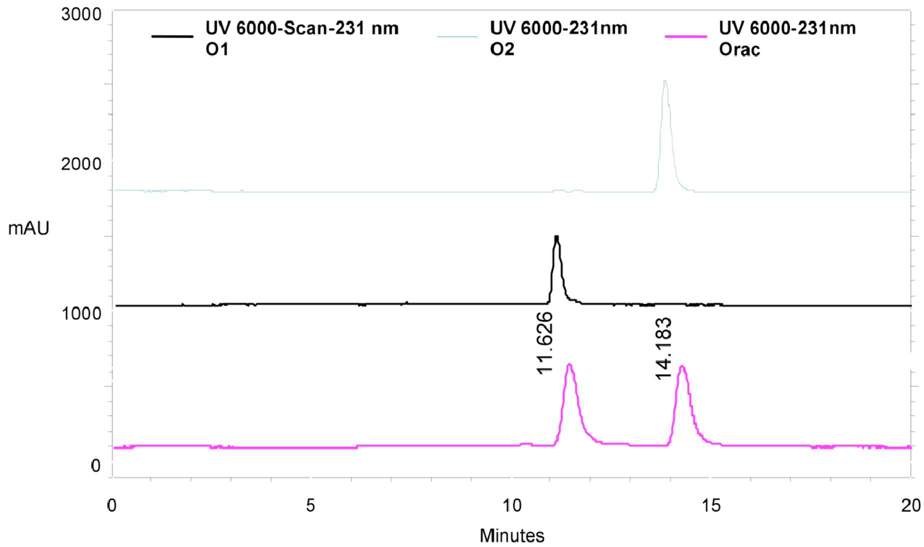
2-Methylnaphthol (**5d**, 16 mg, 0.01 mmol) was submitted to the general procedure A’ for 2.5 h using (–)-**2c** (41.5 mg, 0.01 mmol) to furnish the *ortho*-quinol **6d** (13.3 mg, 76%) in 37% enantiomeric excess:



2-Methylnaphthol (**5d**, 15.8 mg, 0.01 mmol) was submitted to the general procedure A’ for 3 h using (+)-**2c** (41.4 mg, 0.01 mmol) to furnish the *ortho*-quinol **6d** (12.3 mg, 71%) in 37% enantiomeric excess:



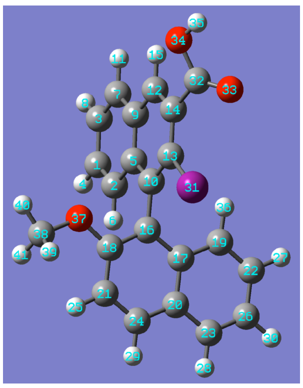
For the sake of the determination of absolute configurations by vibrational circular dichroism, the separation of the two enantiomers of **6d** was undertaken and performed on a Chiralcel AS-H analytical column, eluting with *n*-hexane/*iso*-propanol (8:2) at a flow rate of 0.5 mL/min, with detection at a λ of 231 nm. 29.8 mg of *rac*-**6d** thus afforded (+)-**6d** (12.4 mg, 42%) and (–)-**6d** (11.2 mg, 38 %). (+)-**16**: $[\alpha]_D^{20}$ 244.0° (*c* 0.5, $CHCl_3$), Rt = 11.6 min; (–)-**1d**: $[\alpha]_D^{20}$ –248.9° (*c* 0.5, $CHCl_3$), Rt = 14.2 min.



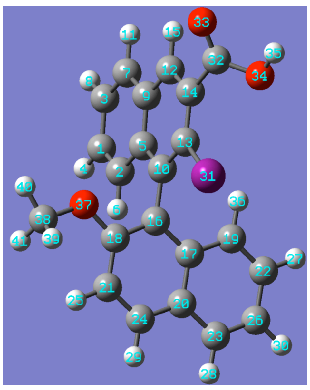
Determination of Absolute Configurations

By Vibrational Circular Dichroism

Vibrational circular dichroism is a well-established method for determination of absolute configuration and solution conformation of chiral molecules.[18] The method entails comparison of observed VCD spectrum with spectra calculated at the density functional theory (DFT) level for conformers of a specified absolute configuration.[19] Because enantiomers have VCD intensities of opposite sign for each vibrational mode, the VCD spectrum provides a unique and rich signature of the absolute configuration. VCD spectrum of the two optical antipodes of 3-iodo-4-(2-methoxynaphthalen-1-yl)naphthalene-2-carboxylic acid **2b**, and of *ortho*-quinol **6d**, were recorded in $CDCl_3$ at a concentration of 8.5 mM and 65 mM, respectively. Calculations of optimized geometry, vibrational frequencies, absorption, and VCD intensities were calculated by Gaussian 03 program at the DFT level with the B3LYP functional and 6-311+G* basis set for the (*R*)-**6d** isomer. On the other hand, LANL2DZ basis set was used for the iodine atom to calculate the two conformations of the (*S*)-**2b** atropisomer. Indeed, **2b** can assume two main conformations that differ by a 180° rotation of the COOH group, labeled **2b-a** (the carbonyl group on the same side of iodine) and **2b-b** (the hydroxyl group on the same side of iodine). The optimized structures and relative Gibbs energies calculated for the two conformers are shown in Scheme 2. **2b-a** and **2b-b** exhibit similar energies and their relative populations are 52 and 48 % at room temperature, respectively.



2b-a: 0. kJ/mol



2b-b: 0.19 kJ/mol

Scheme 2. Optimized structures and relative Gibbs energies of the two conformations of the (*S*)-**2b** atropisomer.

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[18] a) T. B. Freedman, X. Cao, R. K. Dukor, L. A. Nafie, *Chirality*, **2003**, *15*, 743 and references therein; b) T. Buffeteau, D. Cavagnat, A. Bouchet, T. Brotin, *J. Phys. Chem. A*, **2007**, *111*, 1045.

[19] P. J. Stephens, F. J. Delvin, *Chirality*, **2000**, *12*, 172.

The predicted VCD spectrum, tacking into account the relative populations of **2b-a** and **2b-b**, is compared to the experimental spectrum of (–)-**2b** in Figure 3. The predicted VCD spectrum reproduces fairly well the intensity and the sign of the bands observed in the experimental spectrum, allowing the definitive determination of the *S* configuration for (–)-**2b**. Similarly, the predicted VCD spectrum of (*R*)-**6d** is compared to the experimental spectrum of (–)-**6d** in Figure 4. From this comparison, it is clear that the absolute configuration of (–)-**6d** corresponds to the *R* enantiomer.

VCD measurements. IR and VCD spectra were recorded with a ThermoNicolet Nexus 670 FTIR spectrometer equipped with a VCD optical bench.[20] In this optical bench, the light beam was focused by a BaF_2 lens (191 mm focal length) to the sample, passing an optical filter (depending on the studied spectral range), a BaF_2 wire grid polarizer (Specac), and a ZnSe photoelastic modulator (Hinds Instruments, Type II/ZS50). The light was then focused by a ZnSe lens (38.1 mm focal length) onto a 1x1 mm^2 HgCdTe (ThermoNicolet, MCTA* E6032) detector. IR and VCD spectra were recorded at a resolution of 4 cm^{-1}, by coadding 50 scans and 36000 scans (12 h acquisition time), respectively. The sample was held in a variable path length cell with BaF_2 windows. IR and VCD spectra of the two opposite-atropisomers of **2b** and the two opposite-enantiomers of **6d** were measured in CDCl3 at a concentration of 8.5 mM and 65 mM, respectively, and at a path length of 443 μm and 355 μm, respectively. Baseline corrections of the VCD spectrum was performed by subtracting the two opposite-enantiomer VCD spectra of 2b and 6d (recorded under the same experimental concentration) with division by two. In all experiments, the photoelastic modulator was adjusted for a maximum efficiency at 1400 cm^{-1}. Calculations were done with the standard ThermoNicolet software, using Happ and Genzel apodization, de-Haseth phase-correction and a zero-filling factor of one. Calibration spectra were recorded using a birefringent plate (CdSe) and a second BaF_2 wire grid polarizer, following the experimental procedure previously published.[21] Finally, in the presented IR spectra, the solvent absorption was subtracted out.

DFT calculations. The geometry optimizations, vibrational frequencies, absorption, and VCD intensities were calculated by Gaussian 03 program[22] on a SGI Altix XE 1300 of the

[20] T. Buffeteau, F. Lagugné-Labarthet, C. Sourrisseau, *Appl. Spectrosc.* **2005**, *59*, 732.
[21] L. A. Nafie, D. W. Vidrine, In *Fourier Transform Infrared Spectroscopy*, J. R. Ferraro and L. J. Basile, Eds (Academic Press, New York 1982), Vol. 3, pp 83-123.
[22] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M.

Pôle Modélisation of the Institut des Sciences Moléculaires (University Bordeaux I). Calculations of the optimized geometry of (*R*)-**6d** isomer as well as **2b-a** and **2b-b** conformers of the *S* configuration were performed at the density functional theory level using B3LYP functional and 6-311+G* basis set, except for the iodine atom for which LANL2DZ basis set was used. Vibrational frequencies, IR, and VCD intensities were calculated at the same level of theory, utilizing the magnetic field perturbation method with gauge-invariant atomic orbitals.[23] For comparison to experimental data, the calculated frequencies were scaled by 0.978 and the calculated intensities were converted to Lorentzian bands with half-width of 4 cm^{-1}.

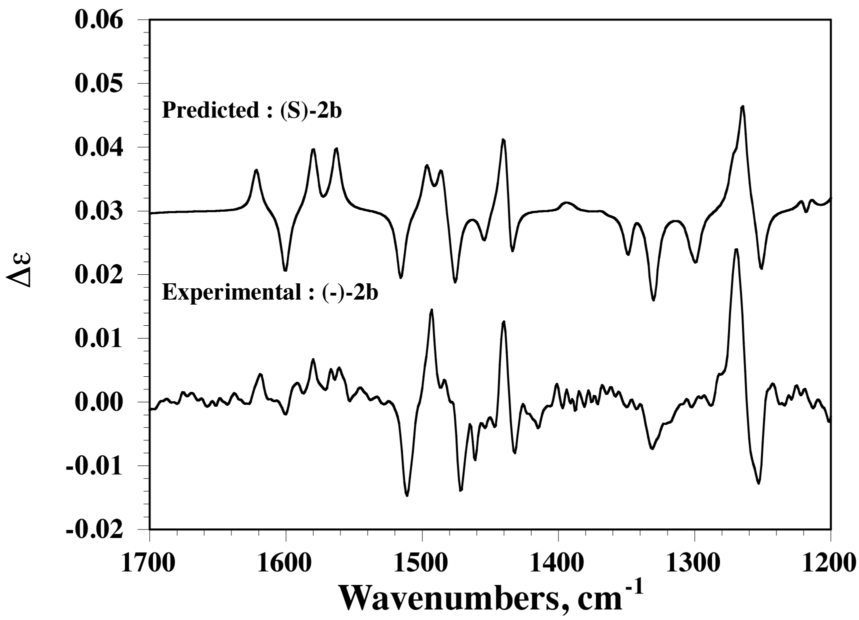


Figure 3. Comparison of the experimental VCD spectrum for (–)-**2b** in $CDCl_3$ solution (8.5 mM, 443 μm path length) with the predicted VCD spectrum of the (*S*)-**2b** configuration.

Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople. *GAUSSIAN 03;* Revision B.04, Gaussian Inc., Pittsburgh, PA, 2003.

[23] J. R. Cheeseman, M. J. Frisch, F. J. Delvin, P. J. Stephens, *Chem. Phys. Lett*. **1996**, *252*, 211.

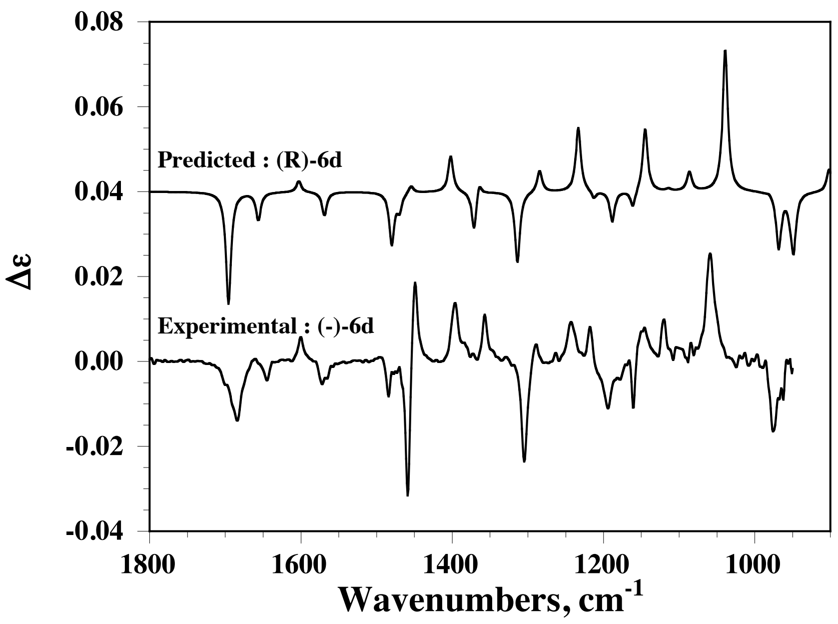


Figure 4. Comparison of the experimental VCD spectrum for (–)-**6d** in $CDCl_3$ solution (65 mM, 355 μm path length) with the predicted VCD spectrum of the (*R*)-**6d** configuration.

Determination of the absolute configuration of (–)-2b

Experimental (–)-**2b**		Calculated (*S*)-**2b**		agreement
Freq. (cm^{-1})	sign	Freq. (cm^{-1})	sign	
1619	+	1622	+	yes
1600	–	1600	–	yes
1580	+	1580	+	yes
1564	+	1564	+	yes
1511	–	1515	–	yes
1493	+	1496	+	yes
1484	+	1485	+	yes
1471	–	1475	–	yes
1460	–	1455	–	yes
1440	+	1440	+	yes
1432	–	1433	–	yes
1415	–	1395	+	no
not observed		1349	–	no
1330	–	1330	–	yes
1302	–	1300	–	yes
1269	+	1265	+	yes
1254	–	1251	–	yes

The bands of the experimental (–)-**2b** compound correlate and agree in sign for most (15/17) of the vibrational modes calculated for the *S* configuration of **2b**. From this comparison, it is clear that the absolute configuration of (–)-2b corresponds to the *S*-enantiomer of **2b**.

Determination of the absolute configuration of (–)-6d

Experimental (–)-**6d**		Calculated (*R*)-**6d**		agreement
Freq. (cm^{-1})	sign	Freq. (cm^{-1})	sign	
1684	–	1694	–	yes
1644	–	1654	–	yes
1599	+	1602	+	yes
1568	–	1568	–	yes
1486	–	1481	–	yes
1460	–	1470	–	yes
1449	+	1454	+	yes
1396	+	1401	+	yes
not observed		1372	–	no
1357	+	1362	+	yes
1304	–	1314	–	yes
1288	+	1285	+	yes
1243	+	1233	+	yes
1219	+	1211	–	no
1193	–	1188	–	yes
1161	–	1161	–	yes
1148	+	1145	+	yes
1121	+	1114	+	yes
not observed		1087	+	no
1058	+	1040	+	yes
974	–	969	–	yes
963	–	950	–	yes

The bands of the experimental (–)-**6d** compound correlate and agree in sign for most (19/22) of the vibrational modes calculated for the *R* configuration of **6d**. From this comparison, it is clear that the absolute configuration of (–)-**6d** corresponds to the *R*-enantiomer of **6d**.

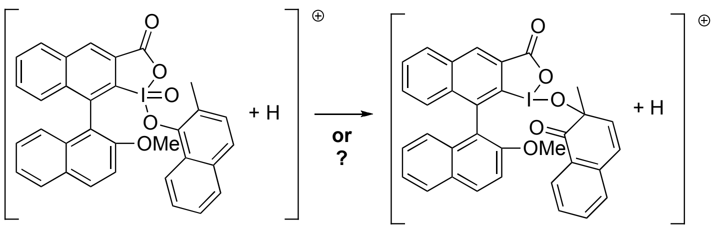
ESI-MS Monitoring of the HPD of 2-Methylnaphthol (5d) into Ortho-Quinol 6d

The general procedure A' was applied. To a stirred solution of partially dried (overnight under high vacuum) and titrated *m*-CPBA (*ca*. 70% w/w, 10.87 mg, 0.063 mmol, 1 equiv) in dry CH_2Cl_2 (0.5 mL) was added the iodoarene *rac*-**2b** (28.6 mg, 0.063 mmol, 1 equiv). After stirring at rt for 1 h, the 2-methylnaphtol (**5d**, 10 mg, 0.063 mmol, 1 equiv) was added under N_2. The mixture was stirred for 3 h until no more evolution of the reaction progress was observed by TLC monitoring (petroleum ether/acetone, 7:1), and it was then cooled down to –90 °C. The resulting precipitate was filtered, washed twice with cold CH_2Cl_2 (–90 °C, 2 × 1

0.1 mL) and the filtrates were evaporated to give a residue, which was purified by column chromatography (petroleum ether/acetone, 7:1) to confirm the formation of the expected *ortho*-quinol **6d** as the sole isolated product.

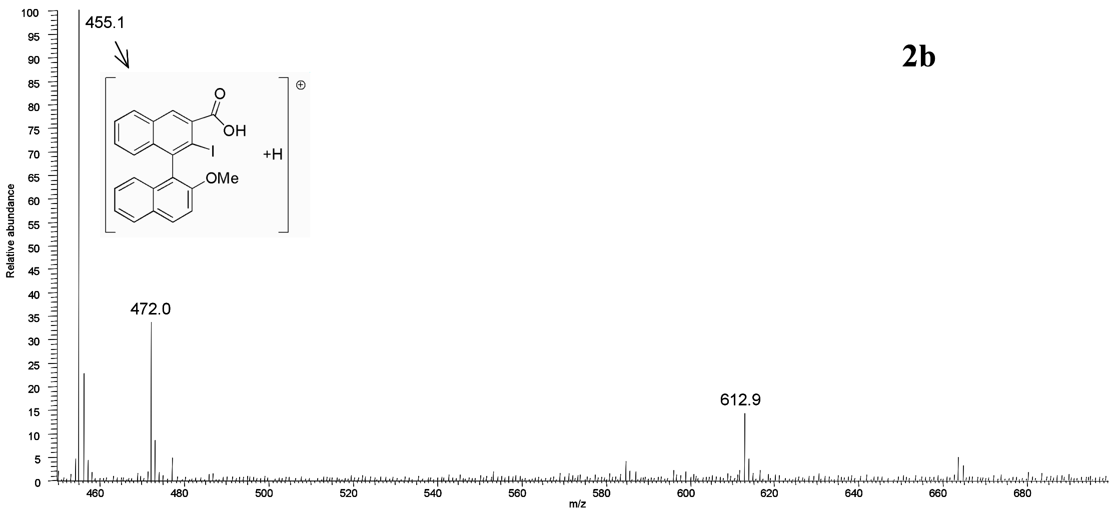
MS and MS/MS analyses were performed on an electrospray ionization-ion trap mass spectrometer LCQ Advantage (Thermo Fisher). The spectrometer was operated in the positive electrospray mode. The spray voltage was set to 4.5 kV, the capillary temperature was 200°C, and the capillary voltage was 10 V. MS/MS spectra were obtained by means of collision-induced dissociation (CID) in the ion-trap, using a normalized collision energy set at 40% of the instrument scale. Aliquots (1 μL) taken from the reaction mixture were diluted in a solution of methanol containing 0.1% of acetic acid (1 mL) and then infused (0.5 mL) with a syringe at a flow rate of 20 μl/min, see spectra a) to e) below.

The most diagnostic peak at *m*/*z* 627 is assigned to the $[M+H]^+$ ion of intermediate **V'** (see Scheme 1 in main text), although it could also be assigned to the subsequent dearomatized product that has the same chemical formula, as shown below:

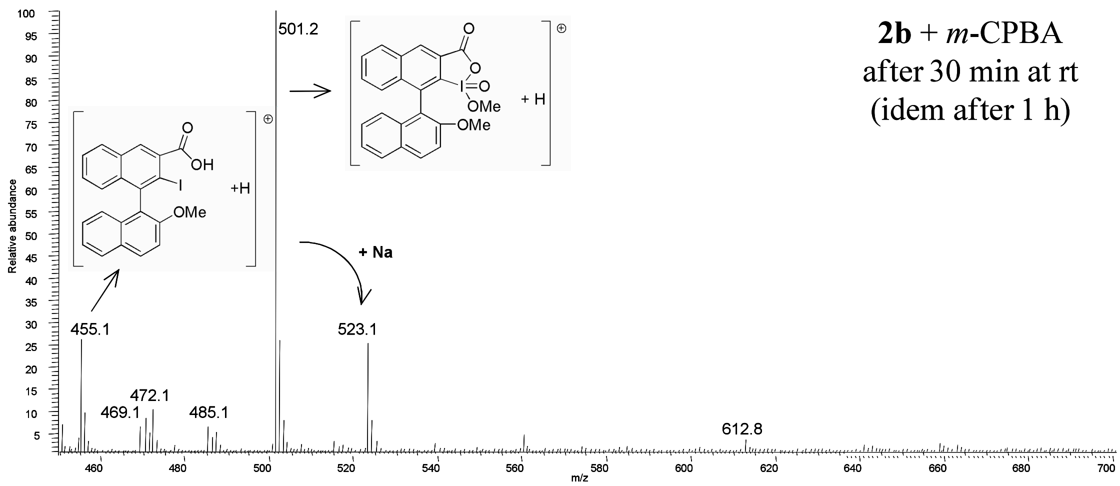


In any case, the elemental composition of the species was confirmed by HRMS (ESI) measurement: calculated for $C_{33}H_{23}O_5I_1$ $[M+H]^+$ 627.0669, found 627.0695. The MS/MS fragmentation spectrum of this ion at *m*/*z* 627 is in agreement with the proposed structure. Major fragments have *m*/*z* values of 595 and 469, which respectively can correspond to $[M–OCH_3]^+$ and $[M–ArO]^+$ ions (ArO = methylnaphthoxy unit). MS/MS spectra of the precursor ions detected at *m*/*z* 501 and 487 in spectra b) to e) also confirm that these species are iodoxy species derived from **2b**. The most intense fragments of the *m*/*z* 501 $[M+H]^+$ ion are fragment ions at *m*/*z* 485 $[M–Me]^+$, 469 $[M–OCH_3]^+$ and 441 $[M–OMe–CO]^+$, and the *m*/*z* 487 $[M+H]^+$ ion fragments to give a prominent peak at *m*/*z* 469 $[M–OH]^+$.

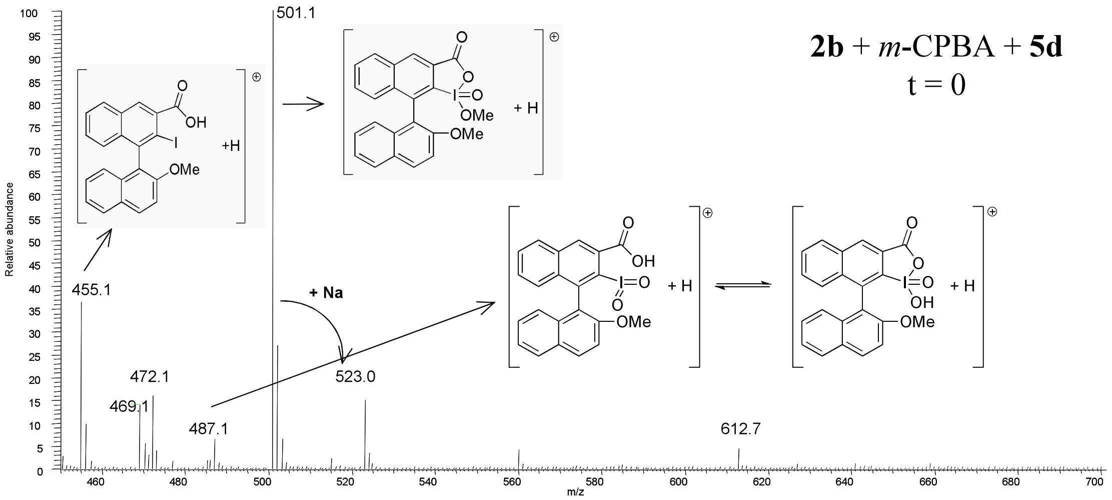
a)


2b
455.1
472.0
612.9
OH
I
OMe
+H
Relative abundance
m/z

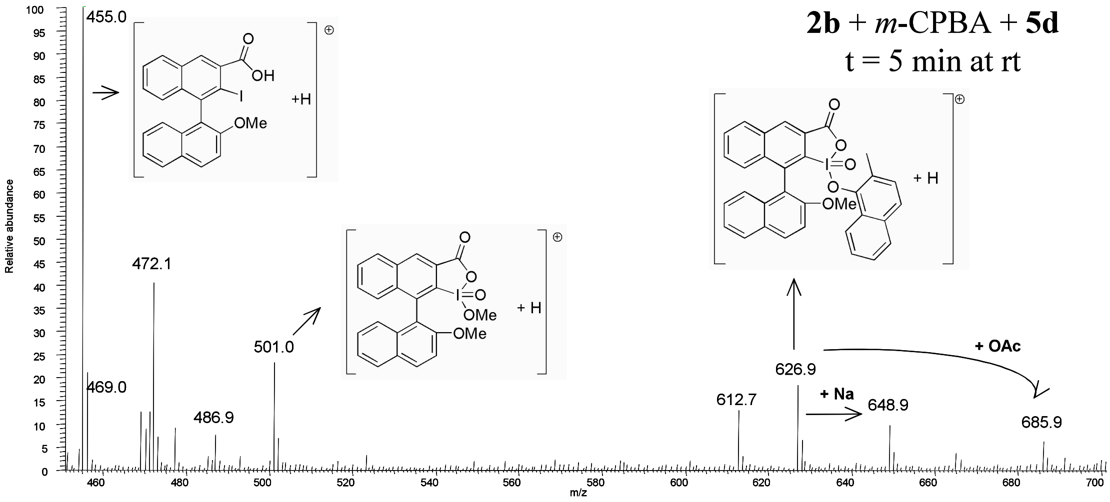
b)


2b + *m*-CPBA
after 30 min at rt
(idem after 1 h)
501.2
455.1
469.1
472.1
485.1
523.1
612.8
+ Na
OH
I
OMe
+H
+ H
Relative abundance
m/z

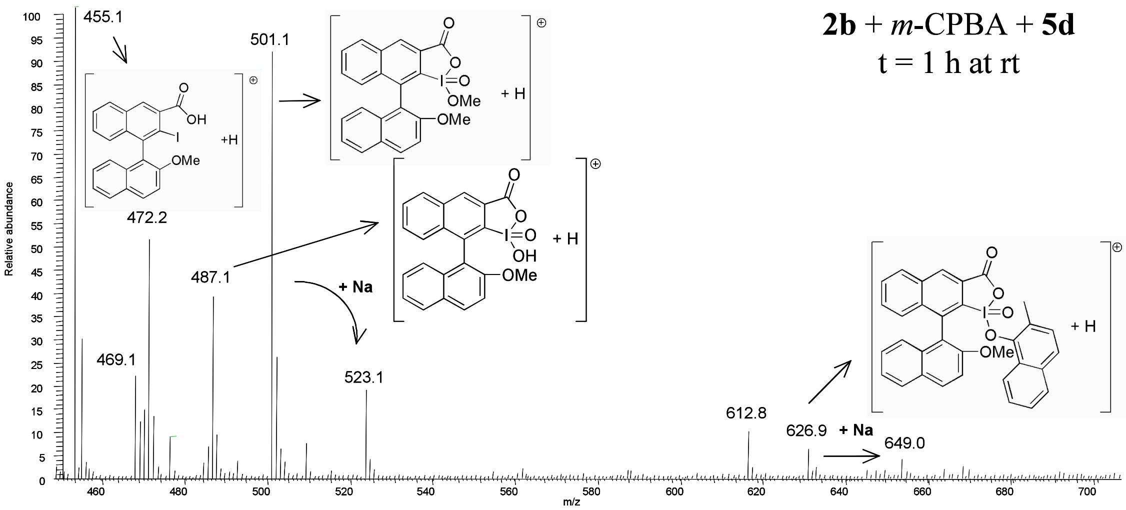
c)


2b + *m*-CPBA + 5d
t = 0
501.1
455.1
469.1
472.1
487.1
523.0
612.7
+ Na
OH
OMe
+H
+ H
Relative abundance
m/z

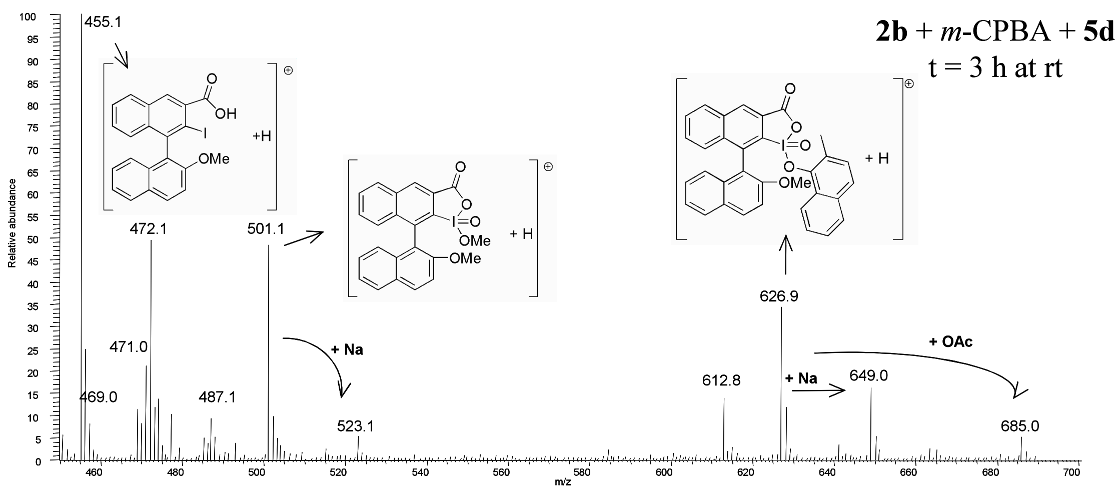
d)

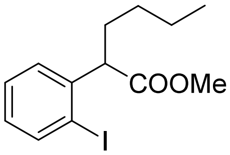

2b + m-CPBA + 5d
t = 5 min at rt
455.0
472.1
469.0
486.9
501.0
612.7
626.9
+ Na
648.9
+ OAc
685.9
OH
I
+H
OMe
OMe
+ H
Relative abundance
m/z

e)


2b + m-CPBA + 5d
t = 1 h at rt
455.1
501.1
472.2
487.1
+ Na
523.1
469.1
612.8
626.9
+ Na
649.0
OH
OMe
+ H
Relative abundance
m/z

f)


2b + m-CPBA + 5d
t = 3 h at rt
455.1
472.1
501.1
471.0
+ Na
469.0
487.1
523.1
626.9
612.8
+ Na
649.0
+ OAc
685.0
OH
OMe
+ H
Relative abundance
m/z



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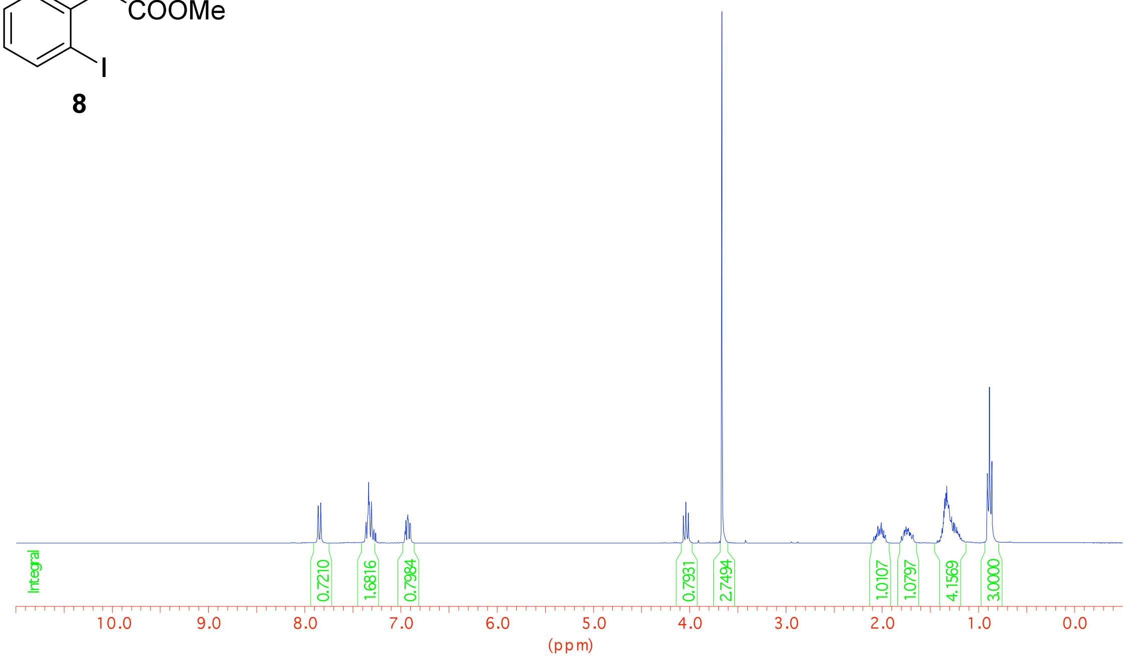
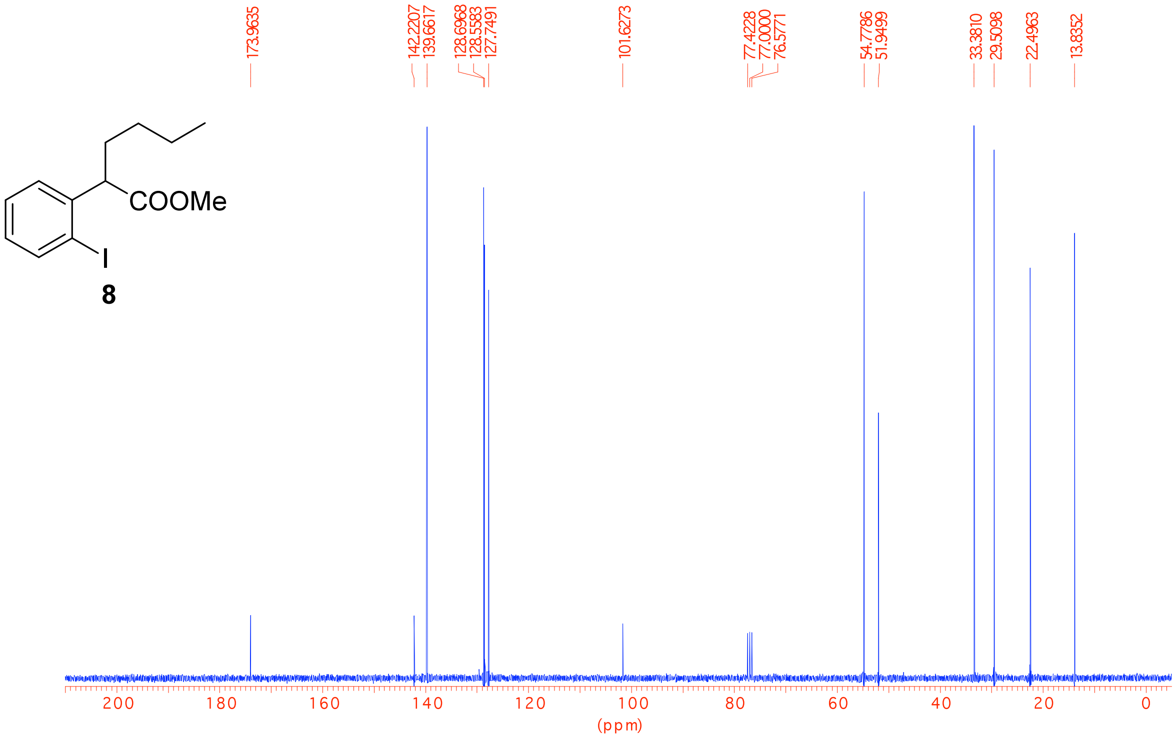


Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13672	2359.29	7.8609	20212646	6.3
2	13677	2358.35	7.8578	22579900	7.0
3	13714	2351.36	7.8345	22041148	6.8
4	13719	2350.42	7.8313	24289164	7.5
5	14454	2211.61	7.3689	8310855	2.6
6	14465	2209.54	7.3619	12726417	3.9
7	14496	2203.68	7.3424	34563332	10.7
8	14507	2201.61	7.3355	36899000	11.4
9	14514	2200.28	7.3311	28075412	8.7
10	14520	2199.15	7.3273	25608152	7.9
11	14551	2193.30	7.3078	21273726	6.6
12	14557	2192.16	7.3040	25186164	7.8
13	14592	2185.55	7.2820	7803768	2.4
14	14598	2184.42	7.2782	8374681	2.6
15	14627	2178.94	7.2600	6033189	1.9
16	15111	2087.54	6.9555	12802614	4.0
17	15122	2085.47	6.9485	13680050	4.2
18	15147	2080.74	6.9328	13415463	4.2
19	15153	2079.61	6.9290	16958024	5.3
20	15158	2078.67	6.9259	17155068	5.3
21	15163	2077.72	6.9227	16645707	5.2
22	15189	2072.81	6.9064	11763938	3.6
23	15200	2070.74	6.8995	11893214	3.7
24	19709	1219.23	4.0623	16524064	5.1
25	19751	1211.30	4.0359	24791112	7.7
26	19789	1204.12	4.0120	18275056	5.7
27	20341	1099.88	3.6647	322693664	100.0
28	22876	621.15	2.0696	4296511	1.3
29	22890	618.51	2.0608	4495546	1.4
30	22900	616.62	2.0545	5684812	1.8

31	22919	613.03	2.0425	10110988	3.1
32	22945	608.12	2.0262	8562384	2.7
33	22971	603.21	2.0098	12267612	3.8
34	22989	599.81	1.9985	8514946	2.6
35	23014	595.09	1.9828	7423848	2.3
36	23034	591.31	1.9702	4128922	1.3
37	23041	589.99	1.9658	4671492	1.4
38	23305	540.14	1.7997	4089130	1.3
39	23334	534.66	1.7814	5608997	1.7
40	23341	533.34	1.7770	6168877	1.9
41	23355	530.69	1.7682	7853689	2.4
42	23370	527.86	1.7588	7856117	2.4
43	23386	524.84	1.7487	9761398	3.0
44	23391	523.89	1.7456	9400610	2.9
45	23405	521.25	1.7367	8237710	2.6
46	23413	519.74	1.7317	7206799	2.2
47	23423	517.85	1.7254	9052034	2.8
48	23442	514.26	1.7135	6442074	2.0
49	23458	511.24	1.7034	6026969	1.9
50	23500	503.31	1.6770	5012952	1.6
51	23996	409.64	1.3649	12258957	3.8
52	24007	407.56	1.3580	19313080	6.0
53	24022	404.73	1.3485	26818780	8.3
54	24038	401.71	1.3385	30289200	9.4
55	24056	398.31	1.3271	34534756	10.7
56	24068	396.05	1.3196	25711380	8.0
57	24088	392.27	1.3070	23065228	7.1
58	24117	386.79	1.2887	13703070	4.2
59	24123	385.66	1.2850	13498651	4.2
60	24134	383.58	1.2781	15880160	4.9
61	24168	377.16	1.2567	12444171	3.9
62	24188	373.38	1.2441	11758315	3.6
63	24219	367.53	1.2246	9595503	3.0
64	24724	272.16	0.9068	42294764	13.1
65	24761	265.17	0.8835	94648800	29.3
66	24799	258.00	0.8596	49464920	15.3



COOMe
I
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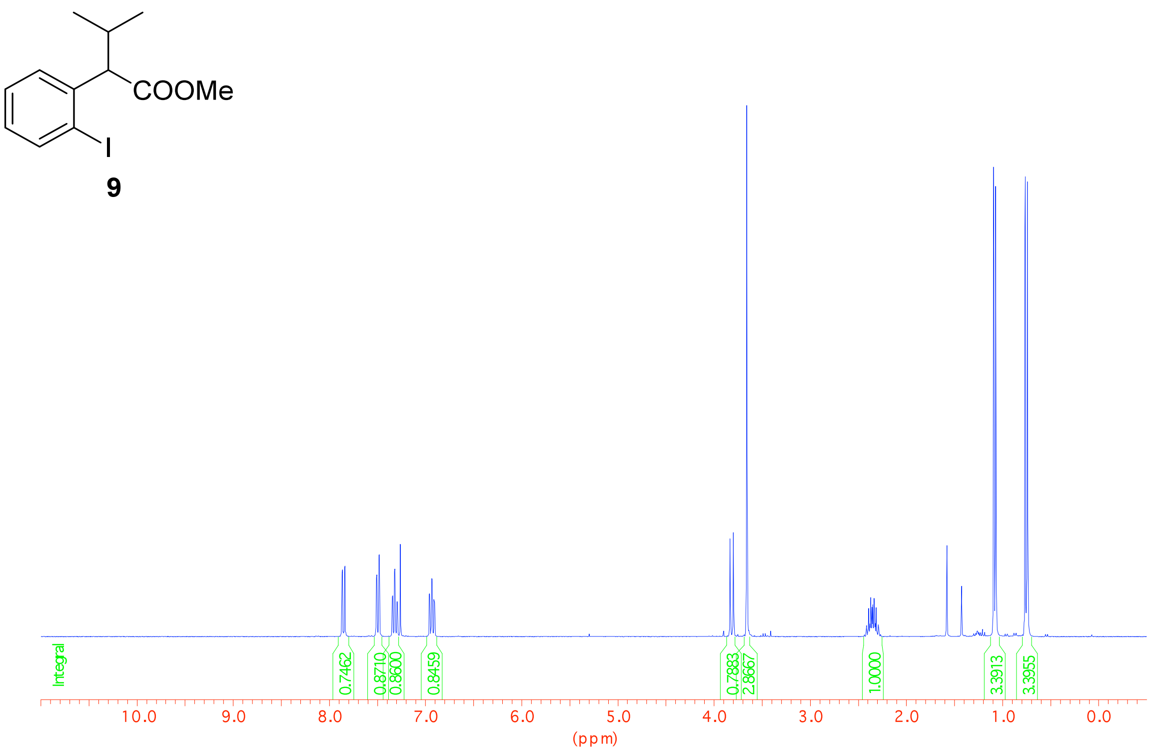
142.2207
139.6617
128.6968
128.5583
127.7491
101.6273
77.4228
77.0000
76.5771
54.7786
51.9499
33.3810
29.5098
22.4963
13.8352
200
180
160
140
120
100
80
60
40
20
0
(ppm)

8

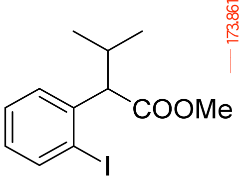


COOMe
I
Integral
0.7462
0.8710
0.8600
0.8459
0.7883
2.8667
1.0000
3.3913
3.3955
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

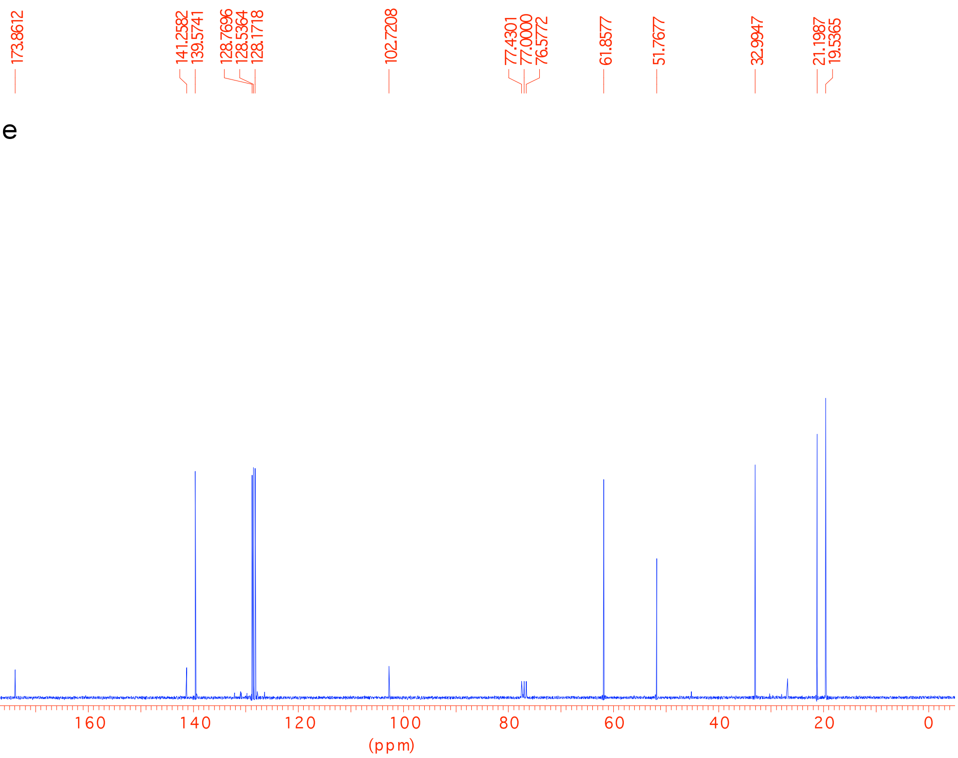
9

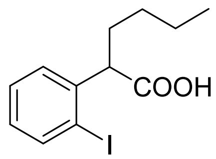
Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13663	2361.18	7.8672	18669148	5.9
2	13670	2359.86	7.8628	19723250	6.3
3	13706	2353.06	7.8401	20297068	6.4
4	13712	2351.93	7.8364	20891564	6.6
5	14233	2253.54	7.5085	17340344	5.5
6	14242	2251.84	7.5029	18250616	5.8
7	14275	2245.61	7.4821	24073754	7.6
8	14284	2243.91	7.4765	24246488	7.7
9	14493	2204.44	7.3449	11758106	3.7
10	14499	2203.31	7.3412	12045981	3.8
11	14533	2196.88	7.3198	19254440	6.1
12	14537	2196.13	7.3173	20008350	6.4
13	14573	2189.33	7.2946	10297104	3.3
14	14579	2188.20	7.2908	10259511	3.3
15	14628	2178.94	7.2600	27321228	8.7
16	15104	2089.05	6.9605	12523219	4.0
17	15113	2087.35	6.9548	12696023	4.0
18	15146	2081.12	6.9341	17125740	5.4
19	15152	2079.99	6.9303	17056604	5.4
20	15184	2073.95	6.9102	10914908	3.5
21	15193	2072.25	6.9045	10480634	3.3
22	20075	1150.30	3.8327	28998056	9.2
23	20130	1139.91	3.7981	30768624	9.8
24	20355	1097.42	3.6565	314799104	100.0
25	24432	327.49	1.0912	139143136	44.2
26	24466	321.07	1.0698	133410336	42.4
27	24952	229.29	0.7640	136172592	43.3
28	24988	222.50	0.7413	134725264	42.8



9





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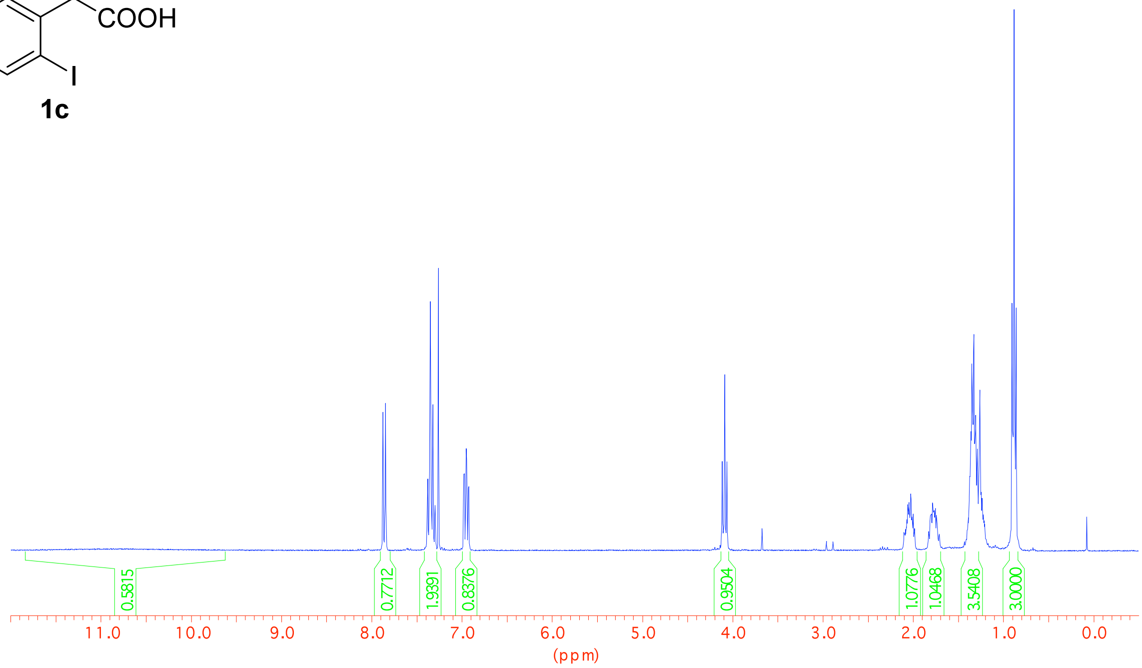
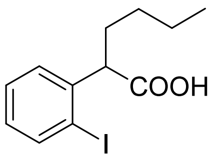


Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	8848	3270.48	10.8969	1025648	0.4
2	13649	2363.82	7.8760	70618544	24.6
3	13654	2362.88	7.8729	73517936	25.6
4	13691	2355.89	7.8496	75856600	26.4
5	13696	2354.95	7.8464	78250784	27.2
6	14444	2213.69	7.3758	38034464	13.2
7	14474	2208.03	7.3569	109851584	38.2
8	14487	2205.57	7.3487	132290360	46.0
9	14495	2204.06	7.3437	86592672	30.1
10	14526	2198.21	7.3242	70023696	24.4
11	14532	2197.07	7.3204	77540840	27.0
12	14628	2178.94	7.2600	149855824	52.1
13	15075	2094.53	6.9787	40468608	14.1
14	15086	2092.45	6.9718	40769096	14.2
15	15111	2087.73	6.9561	41197888	14.3
16	15117	2086.60	6.9523	54101200	18.8
17	15122	2085.65	6.9492	52978636	18.4
18	15128	2084.52	6.9454	47744128	16.6
19	15153	2079.80	6.9297	33191556	11.6
20	15164	2077.72	6.9227	33904632	11.8
21	19628	1234.71	4.1139	47218656	16.4
22	19668	1227.16	4.0888	93467320	32.5
23	19707	1219.79	4.0642	47020084	16.4
24	22826	630.78	2.1017	9566412	3.3
25	22840	628.14	2.0929	10913857	3.8
26	22853	625.68	2.0847	11271590	3.9
27	22866	623.23	2.0765	12480362	4.3
28	22877	621.15	2.0696	16386206	5.7
29	22895	617.75	2.0583	24276402	8.4

30	22912	614.54	2.0476	25419346	8.8
31	22918	613.41	2.0438	23056812	8.0
32	22948	607.74	2.0249	30061904	10.5
33	22966	604.34	2.0136	17756624	6.2
34	22989	600.00	1.9991	19430192	6.8
35	23016	594.90	1.9821	11613068	4.0
36	23260	548.82	1.8286	10081397	3.5
37	23289	543.35	1.8104	18427292	6.4
38	23310	539.38	1.7972	19487850	6.8
39	23330	535.60	1.7846	25242688	8.8
40	23349	532.01	1.7726	20981836	7.3
41	23360	529.94	1.7657	21172308	7.4
42	23378	526.54	1.7544	22352276	7.8
43	23399	522.57	1.7412	18762092	6.5
44	23449	513.13	1.7097	8780676	3.1
45	23957	417.20	1.3901	17238454	6.0
46	23981	412.66	1.3750	39281736	13.7
47	24005	408.13	1.3598	63197888	22.0
48	24020	405.30	1.3504	99104456	34.5
49	24055	398.69	1.3284	114824456	40.0
50	24090	392.08	1.3064	71805776	25.0
51	24116	387.17	1.2900	53949904	18.8
52	24727	271.78	0.9056	131363504	45.7
53	24763	264.99	0.8829	287367424	100.0
54	24801	257.81	0.8590	128815744	44.8



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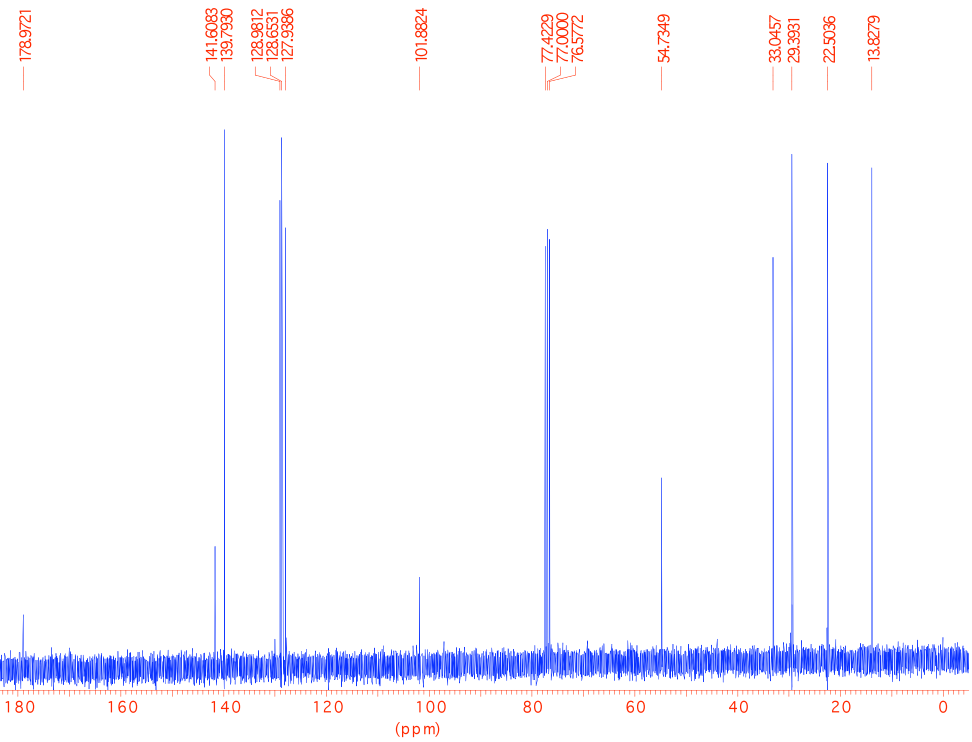
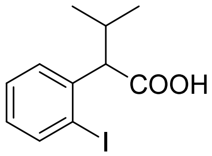
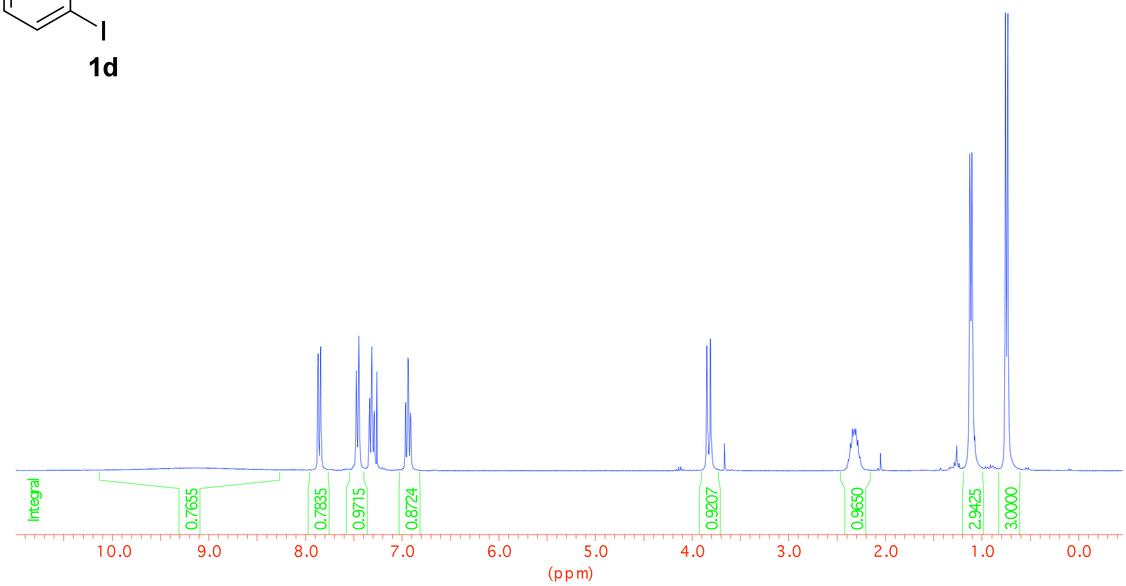


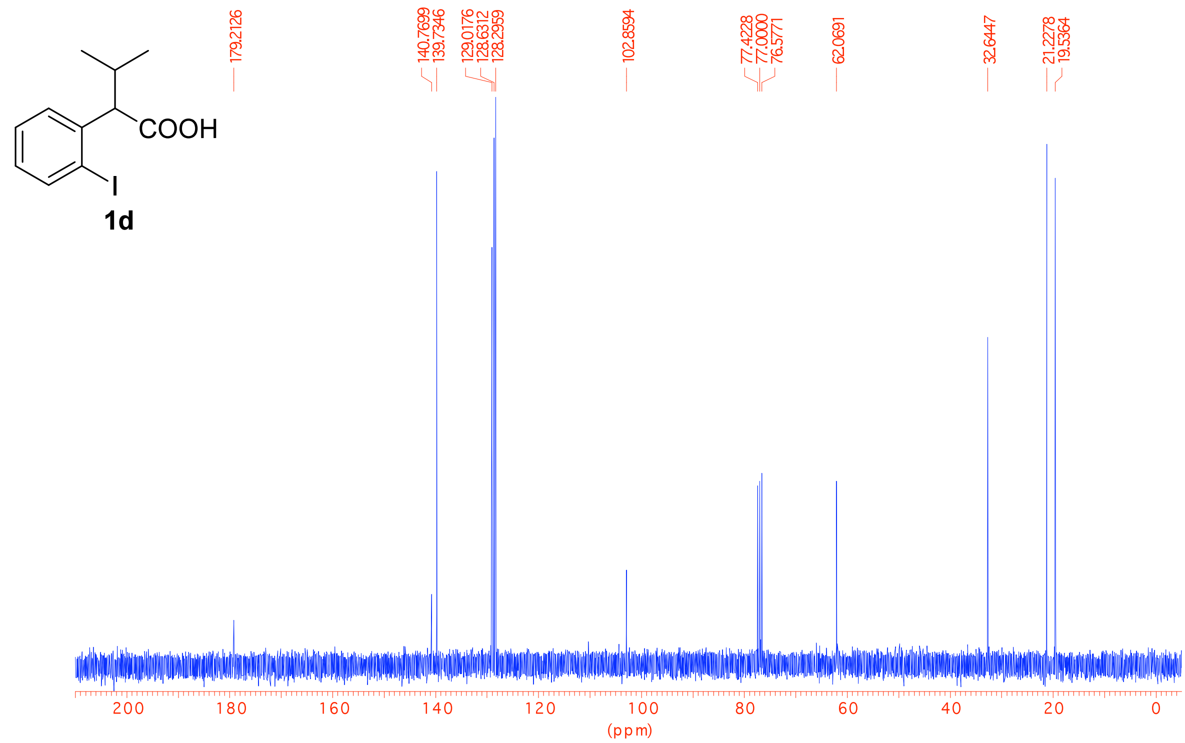


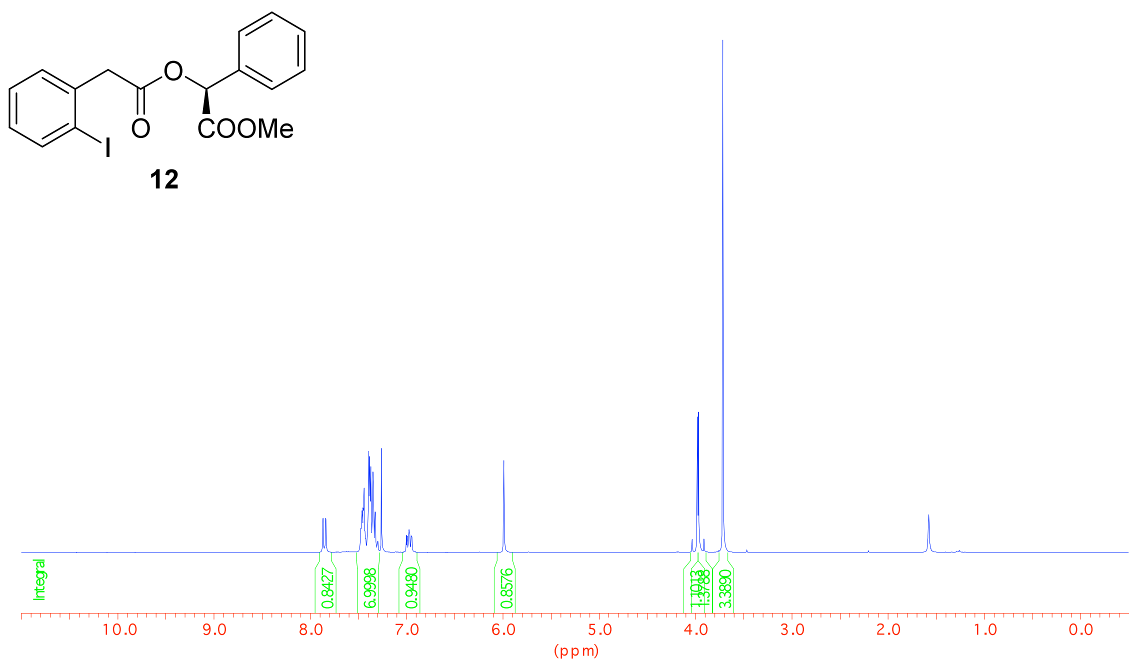
1d



Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	11705	2730.75	9.0986	21136450.6	
2	13664	2360.80	7.8659	88373864	25.5
3	13706	2352.87	7.8395	93818496	27.1
4	14291	2242.40	7.4714	75459320	21.8
5	14332	2234.65	7.4456	101677920	29.4
6	14508	2201.42	7.3349	54856156	15.9
7	14546	2194.24	7.3110	93718544	27.1
8	14587	2186.50	7.2852	45149652	13.0
9	14627	2178.94	7.2600	74727976	21.6
10	15095	2090.56	6.9655	46929864	13.6
11	15102	2089.24	6.9611	51785812	15.0
12	15141	2081.88	6.9366	85035952	24.6
13	15175	2075.46	6.9152	42207172	12.2
14	15183	2073.95	6.9102	43659980	12.6
15	20057	1153.51	3.8434	94509640	27.3
16	20113	1142.93	3.8081	99486064	28.8
17	22378	715.20	2.3830	8200424	2.4
18	22413	708.59	2.3609	20721824	6.0
19	22448	701.98	2.3389	31417904	9.1
20	22482	695.56	2.3175	31323914	9.1
21	22502	691.78	2.3049	31783540	9.2
22	22537	685.17	2.2829	22746892	6.6
23	22571	678.75	2.2615	10547285	3.0
24	24379	337.31	1.1239	239131456	69.1
25	24412	331.08	1.1031	240378160	69.5
26	24965	226.65	0.7552	346032704	100.0
27	25001	219.85	0.7325	345404096	99.8

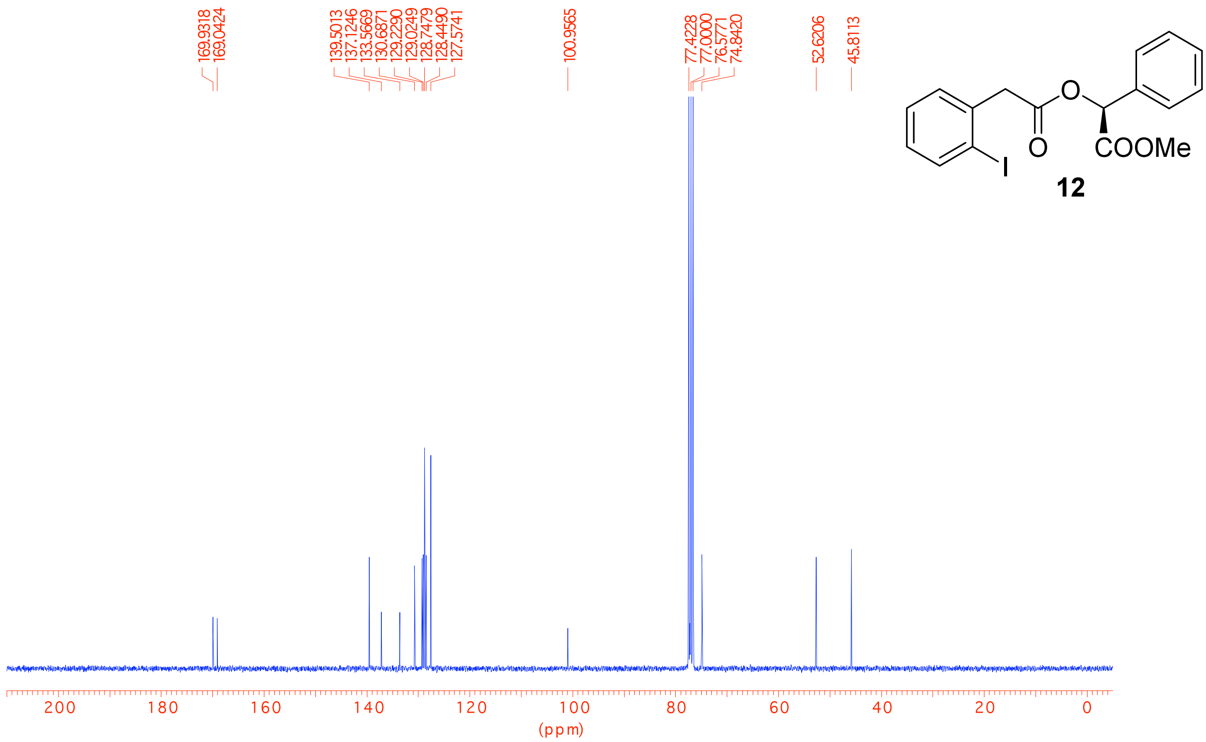




Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13663	2360.99	7.8666	24016934	6.6
2	13704	2353.25	7.8408	24000780	6.6
3	13708	2352.49	7.8382	24038398	6.6
4	14289	2242.77	7.4727	17343446	4.8

5	14308	2239.19	7.4607	29451852	8.1
6	14316	2237.68	7.4557	26184822	7.2
7	14327	2235.60	7.4488	36483480	10.1
8	14340	2233.14	7.4406	45490016	12.5
9	14360	2229.37	7.4280	13854575	3.8
10	14415	2218.98	7.3934	71586368	19.7
11	14434	2215.39	7.3814	67892144	18.7
12	14450	2212.37	7.3714	60840880	16.8
13	14485	2205.76	7.3493	57077364	15.7
14	14492	2204.44	7.3449	50230532	13.9
15	14520	2199.15	7.3273	28832164	8.0
16	14526	2198.02	7.3236	28471258	7.9
17	14561	2191.41	7.3015	7943657	2.2
18	14567	2190.27	7.2978	7779599	2.1
19	14627	2178.94	7.2600	73684424	20.3
20	15038	2101.33	7.0014	12253548	3.4
21	15052	2098.68	6.9926	11493503	3.2
22	15072	2094.91	6.9800	13568364	3.7
23	15080	2093.40	6.9750	16251965	4.5
24	15086	2092.26	6.9712	15932325	4.4
25	15092	2091.13	6.9674	13778400	3.8
26	15115	2086.79	6.9529	11842730	3.3
27	15128	2084.33	6.9448	10924424	3.0
28	16648	1797.29	5.9884	64972624	17.9
29	19754	1210.73	4.0340	9308017	2.6
30	19843	1193.92	3.9780	95998064	26.5
31	19861	1190.52	3.9667	99277288	27.4
32	19950	1173.71	3.9107	9595844	2.6
33	20260	1115.17	3.7156	362503424	100.0



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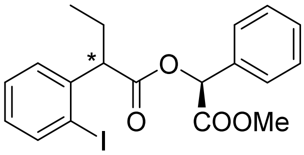
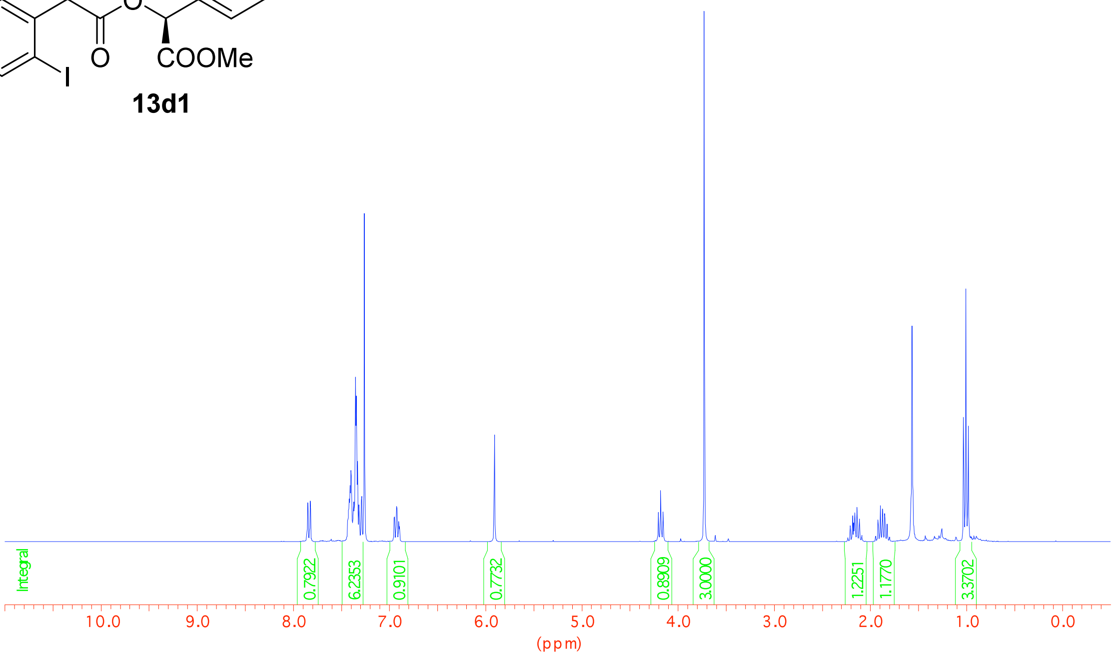


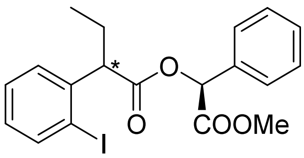
13d1



Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13687	2356.46	7.8515	21555054	7.1
2	13692	2355.52	7.8483	22126970	7.3
3	13729	2348.53	7.8250	23125468	7.6
4	13735	2347.40	7.8213	23177918	7.7
5	14356	2230.12	7.4305	16474897	5.4
6	14375	2226.53	7.4186	24415880	8.1
7	14385	2224.64	7.4123	25801860	8.5
8	14393	2223.13	7.4072	32104958	10.6
9	14407	2220.49	7.3984	40633744	13.4
10	14426	2216.90	7.3865	12609655	4.2
11	14440	2214.26	7.3777	18586636	6.1
12	14450	2212.37	7.3714	22767480	7.5
13	14460	2210.48	7.3651	19616208	6.5
14	14479	2206.89	7.3531	93858640	31.0
15	14493	2204.25	7.3443	83047704	27.4
16	14513	2200.47	7.3317	45917496	15.2
17	14538	2195.75	7.3160	20974992	6.9
18	14543	2194.81	7.3129	19675272	6.5
19	14581	2187.63	7.2889	25885292	8.5
20	14627	2178.94	7.2600	187171648	61.8
21	15115	2086.79	6.9529	13312220	4.4
22	15125	2084.90	6.9467	14126527	4.7
23	15157	2078.86	6.9265	19972652	6.6
24	15163	2077.72	6.9227	19915400	6.6
25	15195	2071.68	6.9026	11597722	3.8
26	15205	2069.79	6.8963	11384827	3.8
27	16779	1772.55	5.9059	61002952	20.1
28	19484	1261.72	4.2039	16718646	5.5
29	19523	1254.35	4.1794	29108080	9.6
30	19563	1246.80	4.1542	17088670	5.6

31	20243	1118.38	3.7263	302764864	100.0
32	22655	662.89	2.2087	9106222	3.0
33	22695	655.33	2.1835	14908802	4.9
34	22714	651.74	2.1715	10865151	3.6
35	22729	648.91	2.1621	16472119	5.4
36	22768	641.55	2.1376	19517680	6.4
37	22808	633.99	2.1124	12935242	4.3
38	23115	576.02	1.9192	12469835	4.1
39	23153	568.84	1.8953	20485974	6.8
40	23191	561.66	1.8714	18542192	6.1
41	23226	555.05	1.8494	16128934	5.3
42	23265	547.69	1.8248	10151530	3.4
43	23676	470.07	1.5662	123090144	40.7
44	24528	309.18	1.0301	70920624	23.4
45	24567	301.81	1.0056	144264848	47.6
46	24606	294.45	0.9811	65857408	21.8



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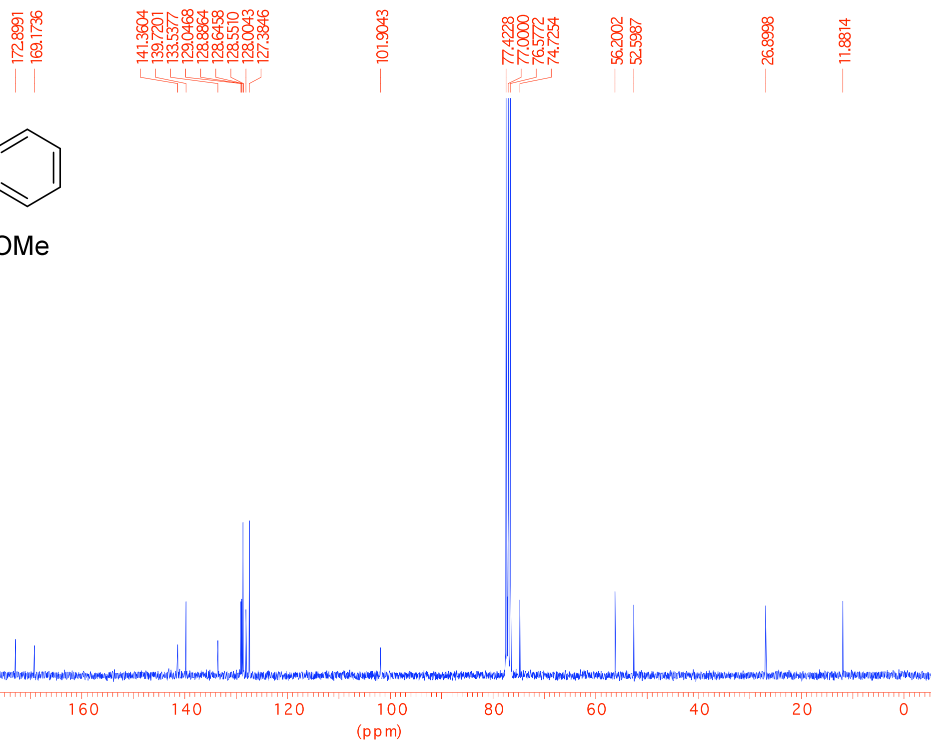
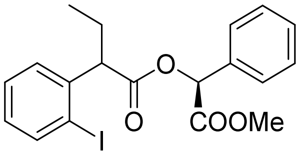
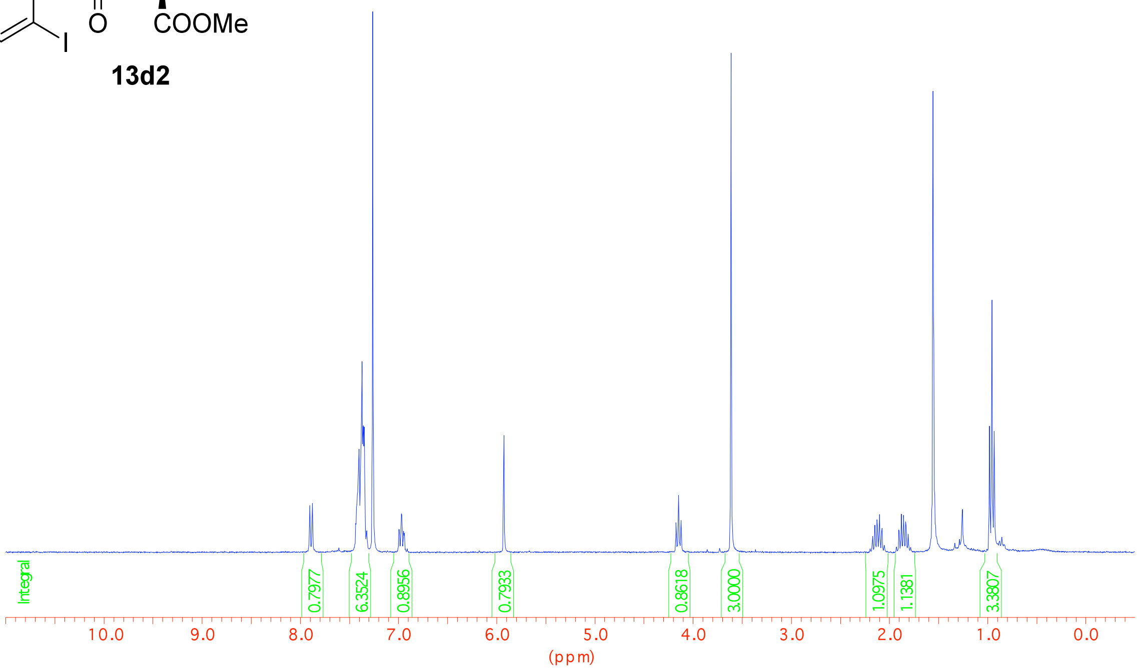


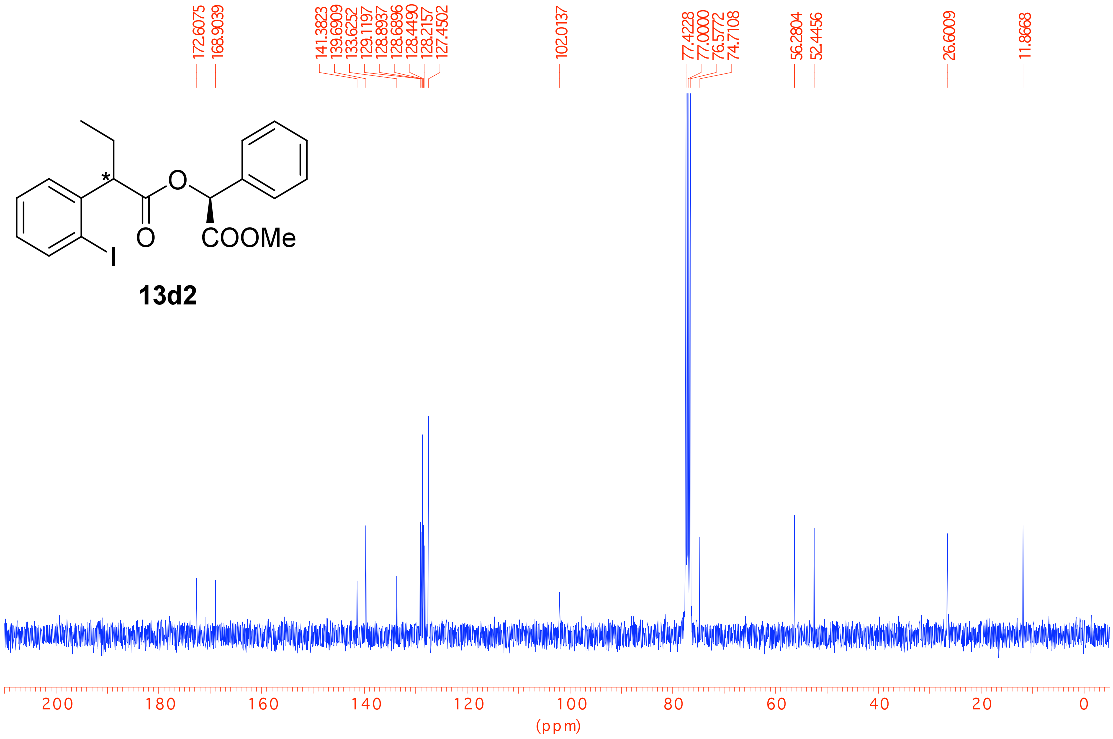


13d2



Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13610	2371.38	7.9012	31727050	8.6
2	13652	2363.45	7.8747	33336724	9.0
3	14403	2221.62	7.4022	70399680	19.1
4	14431	2216.34	7.3846	69000032	18.7
5	14454	2211.99	7.3701	130103416	35.2
6	14473	2208.40	7.3582	86465272	23.4
7	14490	2205.19	7.3475	85599728	23.2
8	14528	2198.02	7.3236	14534586	3.9
9	14629	2178.94	7.2600	369330784	100.0
10	15050	2099.44	6.9951	15508383	4.2
11	15060	2097.55	6.9888	15460554	4.2
12	15093	2091.32	6.9680	26438300	7.2
13	15128	2084.71	6.9460	14320147	3.9
14	15138	2082.82	6.9397	13002536	3.5
15	16752	1778.02	5.9242	79822144	21.6
16	19539	1251.71	4.1706	20140412	5.5
17	19578	1244.34	4.1460	38790624	10.5
18	19617	1236.98	4.1215	21574116	5.8
19	20428	1083.82	3.6112	340937952	92.3
20	22717	651.55	2.1709	10954715	3.0
21	22756	644.19	2.1464	18529930	5.0
22	22791	637.58	2.1243	22333884	6.0
23	22830	630.21	2.0998	25677390	7.0
24	22869	622.85	2.0753	16375468	4.4
25	23144	570.92	1.9022	15157173	4.1
26	23183	563.55	1.8777	25915482	7.0
27	23220	556.56	1.8544	25058418	6.8
28	23256	549.77	1.8318	20772296	5.6
29	23295	542.40	1.8072	12301098	3.3
30	23698	466.30	1.5536	314868672	85.3
31	24610	294.07	0.9798	86091024	23.3

32	24649	286.70	0.9553	172371376	46.7
33	24688	279.34	0.9307	82653376	22.4



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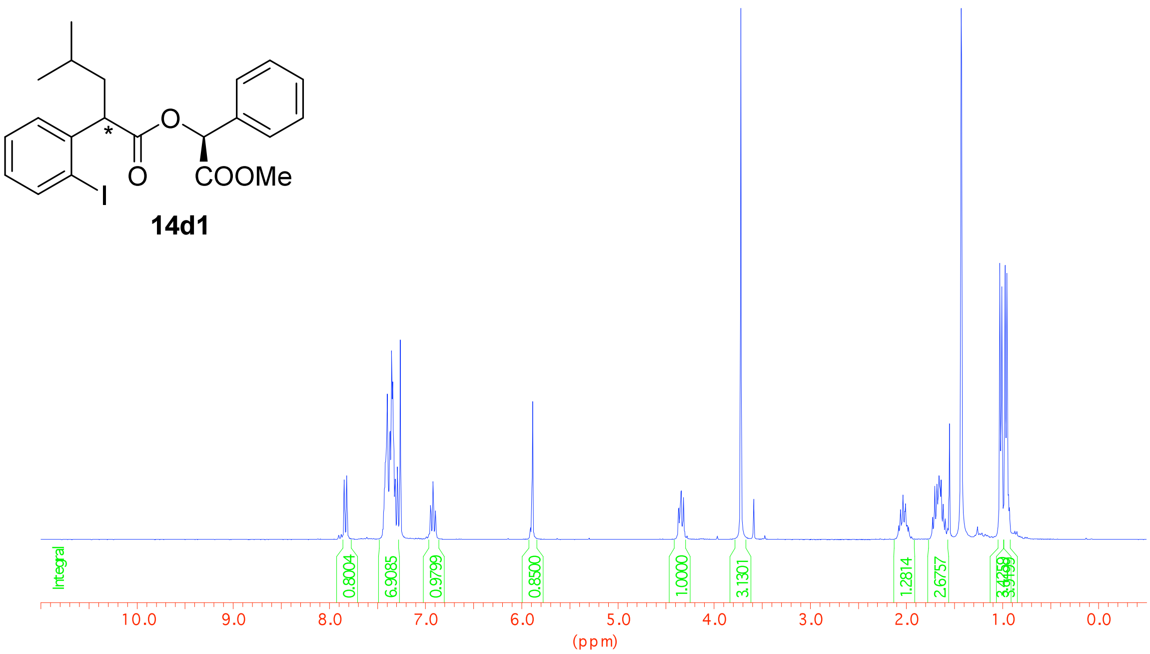
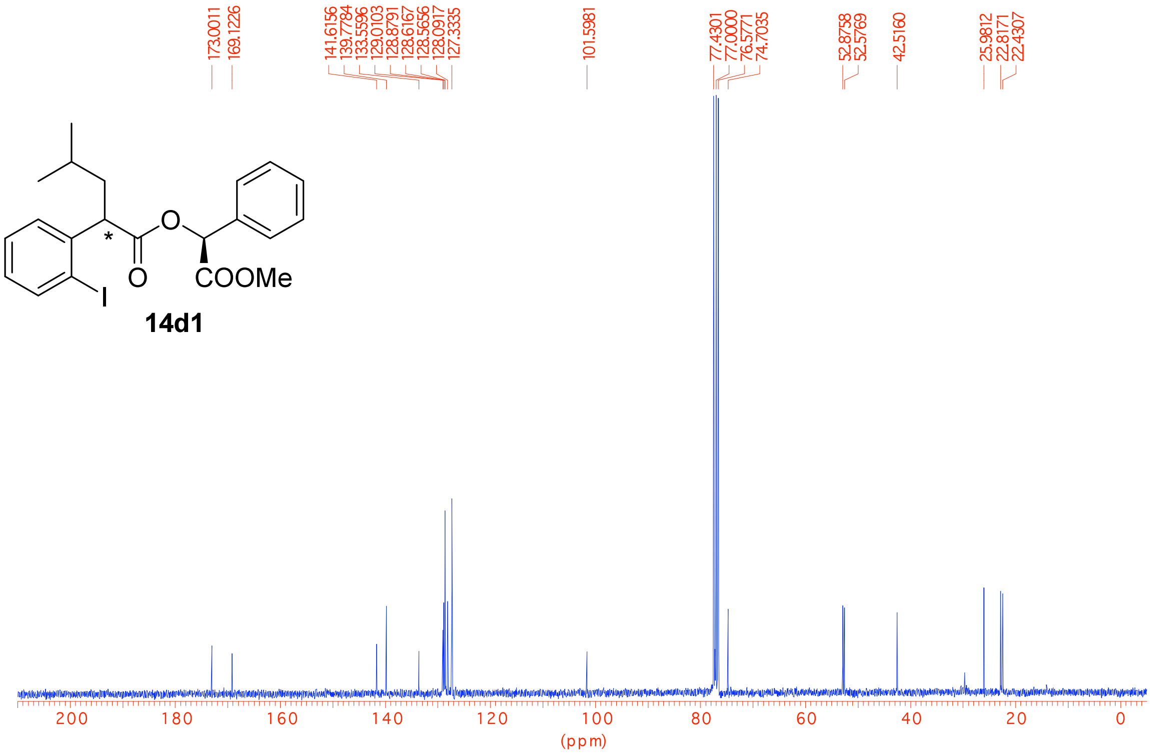


14d1

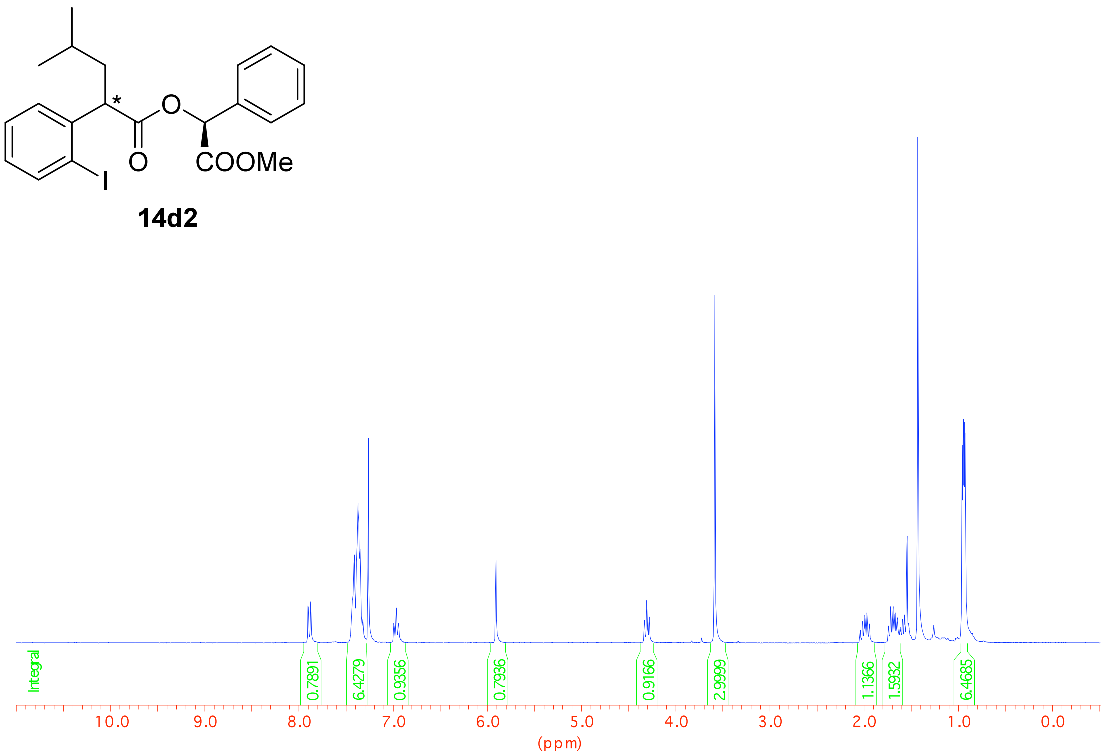
Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13701	2354.00	7.8433	15412142	10.0
2	13743	2346.07	7.8169	16490721	10.7
3	14411	2219.92	7.3965	37713336	24.4
4	14458	2211.05	7.3670	28038648	18.1
5	14484	2206.14	7.3506	48916900	31.6
6	14499	2203.31	7.3412	40882864	26.4
7	14515	2200.28	7.3311	26396416	17.1
8	14518	2199.72	7.3292	26238098	17.0
9	14541	2195.37	7.3147	15632048	10.1
10	14581	2187.82	7.2896	18863900	12.2
11	14628	2178.94	7.2600	51755336	33.5
12	15127	2084.71	6.9460	8781608	5.7
13	15168	2076.97	6.9202	15059141	9.7
14	15206	2069.79	6.8963	7394430	4.8
15	16811	1766.69	5.8864	35732932	23.1
16	19227	1310.44	4.3662	8161242	5.3
17	19269	1302.51	4.3398	12620355	8.2
18	19305	1295.71	4.3172	10841700	7.0
19	20255	1116.31	3.7194	154614320	100.0
20	22863	623.79	2.0784	3622520	2.3
21	22894	617.94	2.0589	7760357	5.0
22	22910	614.92	2.0488	3765363	2.4
23	22934	610.39	2.0337	11523636	7.5
24	22965	604.53	2.0142	7361785	4.8
25	22976	602.45	2.0073	9201855	6.0
26	23005	596.98	1.9891	3749138	2.4
27	23027	592.82	1.9752	3317635	2.1
28	23075	583.76	1.9450	696552	0.5
29	23424	517.85	1.7254	5794685	3.7
30	23461	510.86	1.7021	13855362	9.0
31	23497	504.07	1.6795	14383239	9.3
32	23517	500.29	1.6669	11072684	7.2
33	23532	497.46	1.6575	16536729	10.7
34	23546	494.81	1.6487	13748194	8.9
35	23565	491.22	1.6367	15497750	10.0
36	23600	484.61	1.6147	9186978	5.9
37	23635	478.00	1.5927	5377258	3.5
38	23671	471.21	1.5700	2964682	1.9
39	24534	308.23	1.0270	71665632	46.4
40	24567	302.00	1.0062	65529168	42.4
41	24620	291.99	0.9729	71132304	46.0
42	24653	285.76	0.9521	69098528	44.7

14d1



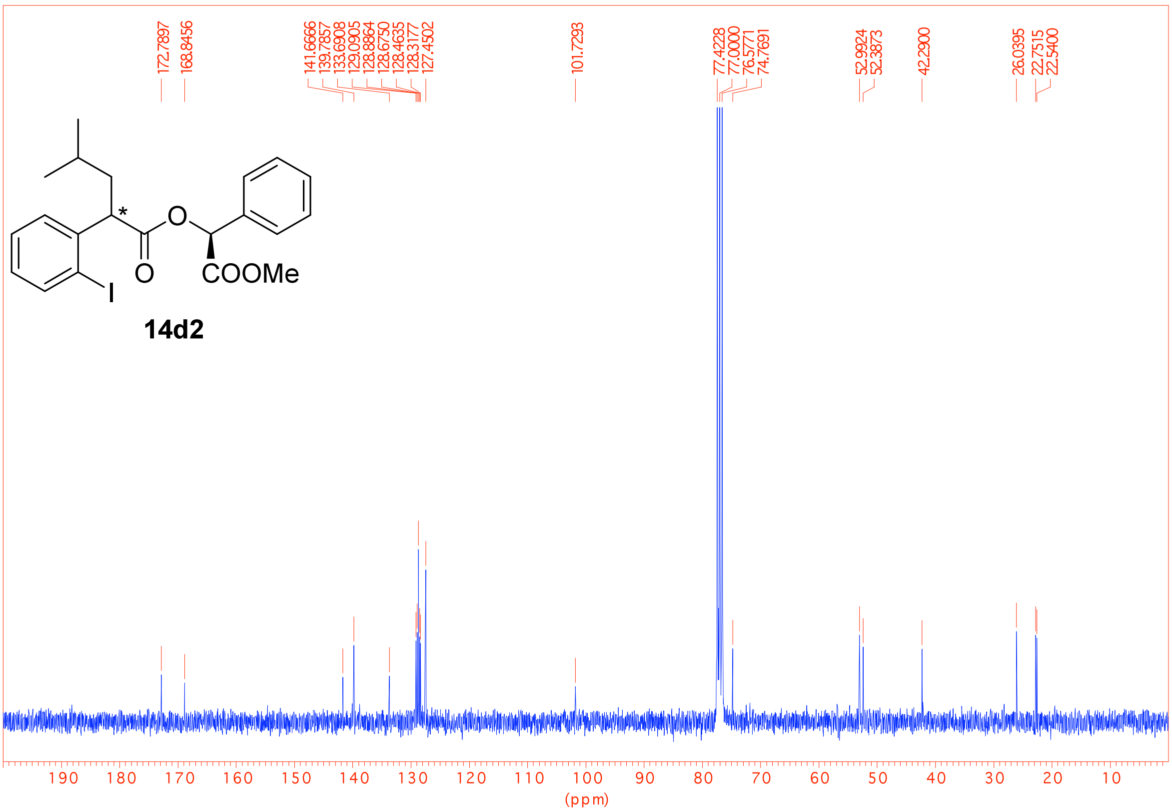
14d2

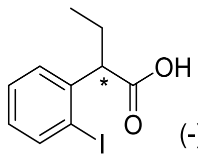


Peak Picking results:

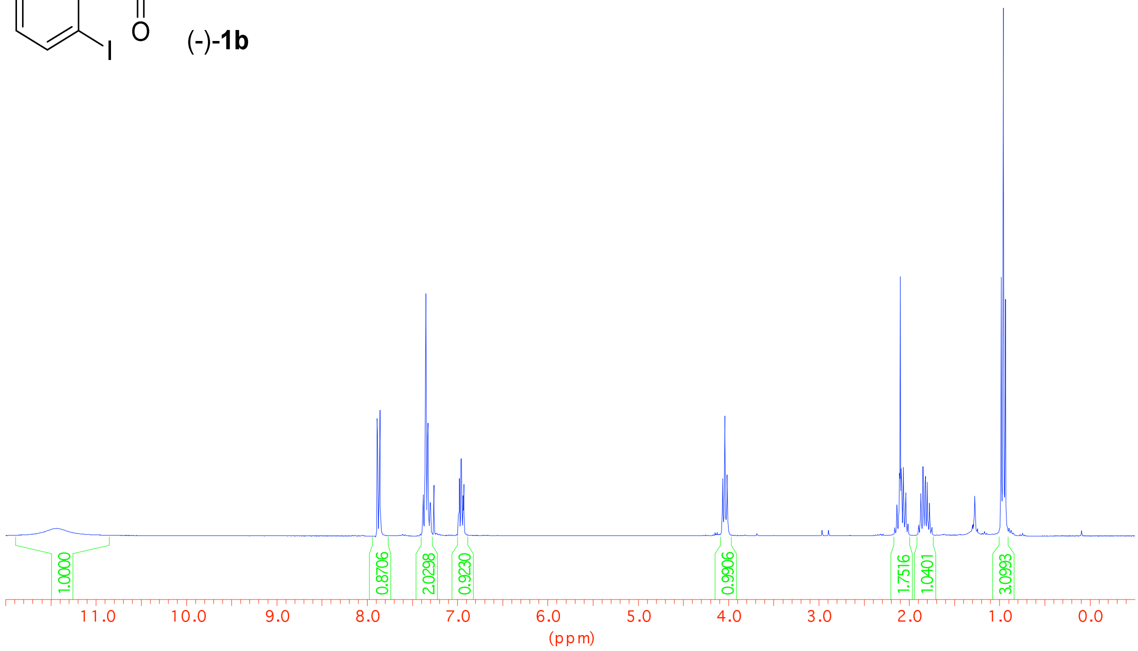
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	7619	2371.20	7.9005	33684880	7.3
2	7661	2363.27	7.8741	37371844	8.1
3	8367	2229.94	7.4299	40448268	8.8

4	8397	2224.28	7.4110	80081072	17.4
5	8458	2212.76	7.3726	126864256	27.6
6	8471	2210.30	7.3644	117019496	25.4
7	8493	2206.15	7.3506	84934752	18.5
8	8542	2196.89	7.3198	21514826	4.7
9	8637	2178.95	7.2600	186232160	40.5
10	9063	2098.50	6.9920	17430856	3.8
11	9105	2090.57	6.9655	31667930	6.9
12	9143	2083.40	6.9416	17622322	3.8
13	10789	1772.55	5.9059	74631520	16.2
14	13295	1299.31	4.3291	20652608	4.5
15	13333	1292.13	4.3052	38541912	8.4
16	13375	1284.20	4.2788	23667356	5.1
17	14479	1075.71	3.5841	316157664	68.7
18	16936	611.72	2.0382	11251793	2.4
19	16974	604.54	2.0143	19433006	4.2
20	17010	597.74	1.9916	25197402	5.5
21	17046	590.94	1.9689	27445532	6.0
22	17087	583.20	1.9432	17314056	3.8
23	17413	521.64	1.7380	15162735	3.3
24	17450	514.65	1.7147	32838062	7.1
25	17486	507.85	1.6921	32753152	7.1
26	17521	501.24	1.6701	27180012	5.9
27	17557	494.44	1.6474	22887368	5.0
28	17906	428.53	1.4278	460173056	100.0
29	18653	287.47	0.9578	183363968	39.8
30	18670	284.26	0.9471	203444448	44.2
31	18687	281.05	0.9364	200961392	43.7
32	18703	278.02	0.9263	191092432	41.5





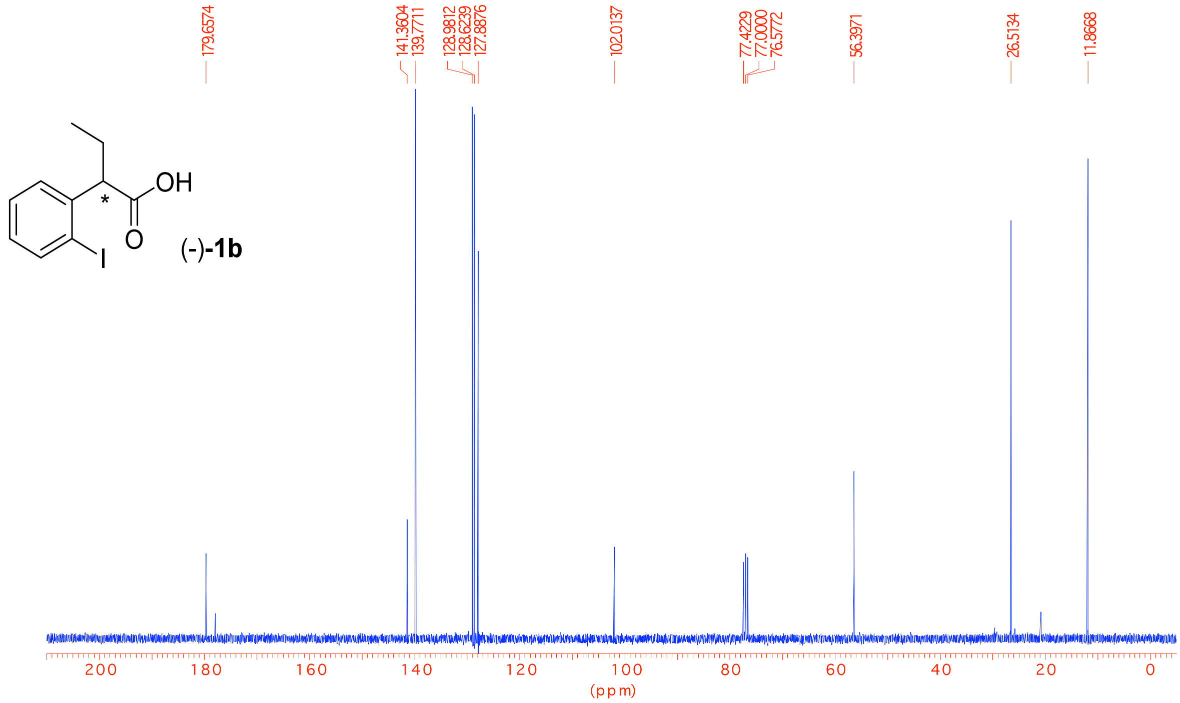
(-)-**1b**

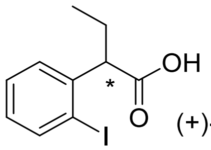


Peak Picking results:

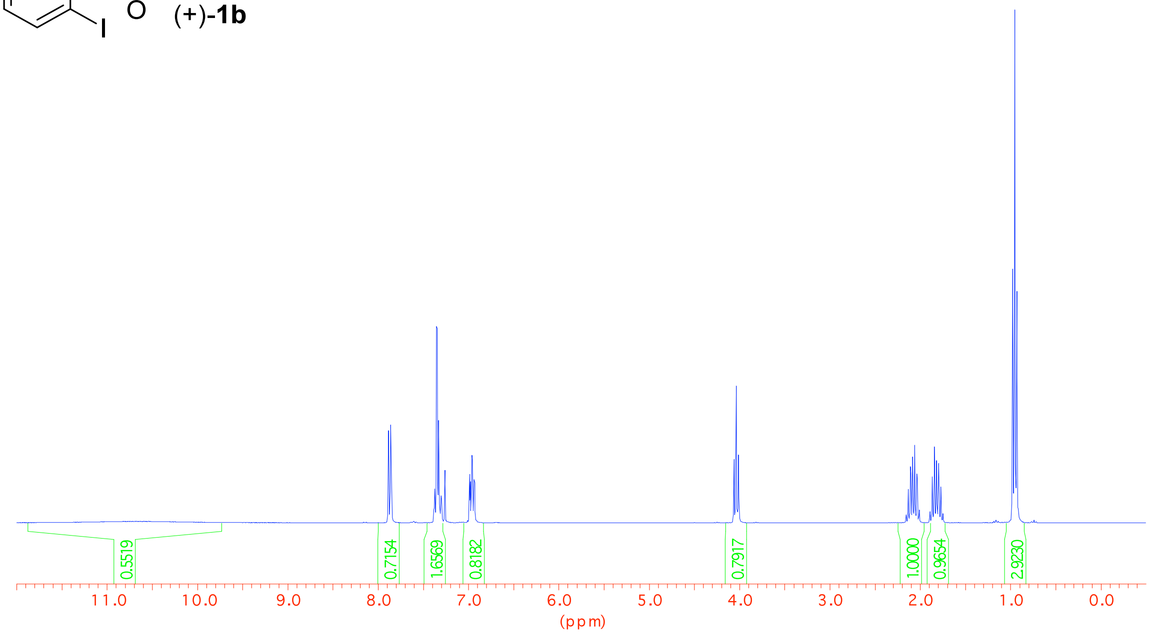
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	7987	3433.07	11.4386	7160446	1.4
2	13632	2367.04	7.8867	117649064	22.2
3	13636	2366.28	7.8842	116079248	21.9
4	13673	2359.29	7.8609	124826512	23.6
5	13679	2358.16	7.8571	125967408	23.8
6	14433	2215.77	7.3827	24520796	4.6
7	14445	2213.50	7.3751	41003600	7.7
8	14475	2207.84	7.3563	162995568	30.8
9	14486	2205.76	7.3493	242847728	45.8
10	14518	2199.72	7.3292	106719856	20.1
11	14524	2198.58	7.3254	112938224	21.3
12	14560	2191.79	7.3028	33387588	6.3
13	14565	2190.84	7.2996	33119584	6.3
14	14628	2178.94	7.2600	50682760	9.6
15	15065	2096.42	6.9850	56705792	10.7
16	15077	2094.15	6.9775	57602944	10.9
17	15100	2089.81	6.9630	54185720	10.2
18	15107	2088.49	6.9586	77079952	14.5
19	15112	2087.54	6.9555	77186280	14.6
20	15119	2086.22	6.9511	66614240	12.6
21	15143	2081.69	6.9360	47135600	8.9
22	15154	2079.61	6.9290	51146288	9.7
23	19708	1219.60	4.0636	57274676	10.8
24	19747	1212.24	4.0390	120222200	22.7
25	19787	1204.69	4.0139	61132400	11.5
26	22775	640.41	2.1338	30665220	5.8
27	22815	632.86	2.1086	62636428	11.8
28	22830	630.03	2.0992	260063568	49.1
29	22849	626.44	2.0872	67428048	12.7
30	22887	619.26	2.0633	68530504	12.9
31	22926	611.90	2.0388	42794664	8.1

32	23195	561.10	1.8695	42175400	8.0
33	23234	553.73	1.8450	69289152	13.1
34	23272	546.56	1.8211	59282120	11.2
35	23307	539.95	1.7990	53349132	10.1
36	23346	532.58	1.7745	32365876	6.1
37	24605	294.82	0.9823	259566160	49.0
38	24644	287.46	0.9578	529777312	100.0
39	24683	280.09	0.9332	237227920	44.8





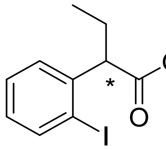
(+)-**1b**



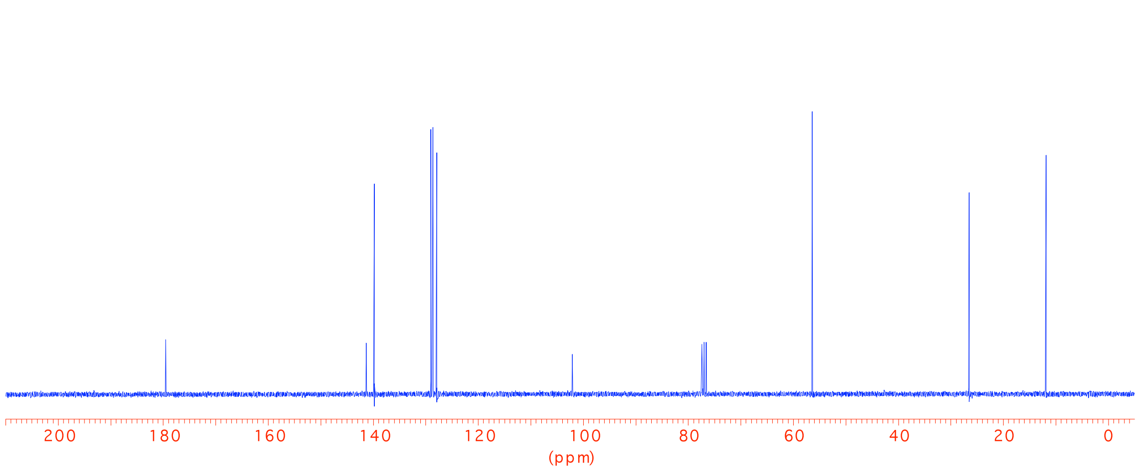
Peak Picking results:

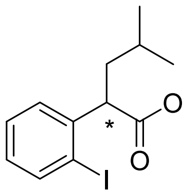
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	9175	3208.72	10.6911	949130	0.3
2	13635	2366.47	7.8848	61697436	17.9
3	13677	2358.54	7.8584	65661512	19.1
4	14452	2212.18	7.3707	22675258	6.6
5	14482	2206.52	7.3519	131534480	38.2
6	14492	2204.63	7.3456	130259936	37.9
7	14519	2199.53	7.3286	68529160	19.9
8	14524	2198.58	7.3254	59054224	17.2
9	14560	2191.79	7.3028	18246920	5.3
10	14628	2178.94	7.2600	35096672	10.2
11	15063	2096.80	6.9863	32502874	9.4
12	15077	2094.15	6.9775	30343084	8.8
13	15098	2090.19	6.9643	36294048	10.6
14	15106	2088.68	6.9592	45312304	13.2
15	15110	2087.92	6.9567	42613912	12.4
16	15118	2086.41	6.9517	33640268	9.8
17	15140	2082.25	6.9378	28967096	8.4
18	15153	2079.80	6.9297	26921090	7.8
19	19714	1218.47	4.0598	42429992	12.3
20	19753	1211.11	4.0353	91561168	26.6
21	19793	1203.55	4.0101	45630288	13.3
22	22781	639.28	2.1300	22561220	6.6
23	22820	631.91	2.1055	37753812	11.0
24	22855	625.30	2.0834	44215704	12.9
25	22893	618.13	2.0595	52040664	15.1
26	22932	610.76	2.0350	32851290	9.6
27	23201	559.96	1.8657	30991608	9.0
28	23241	552.41	1.8406	50843256	14.8
29	23279	545.23	1.8167	41762956	12.1
30	23314	538.62	1.7946	39797536	11.6
31	23353	531.26	1.7701	24058830	7.0

32	24613	293.31	0.9773	170025552	49.4
33	24652	285.95	0.9527	343981056	100.0
34	24691	278.58	0.9282	155140864	45.1



(+)-**1b**





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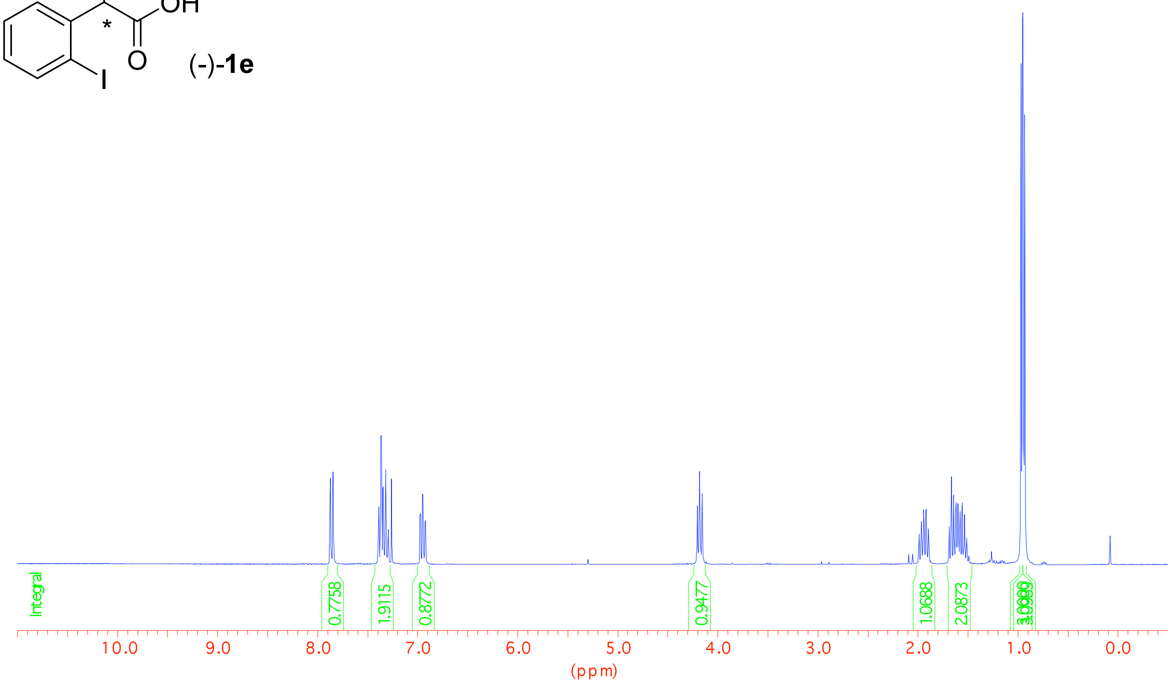
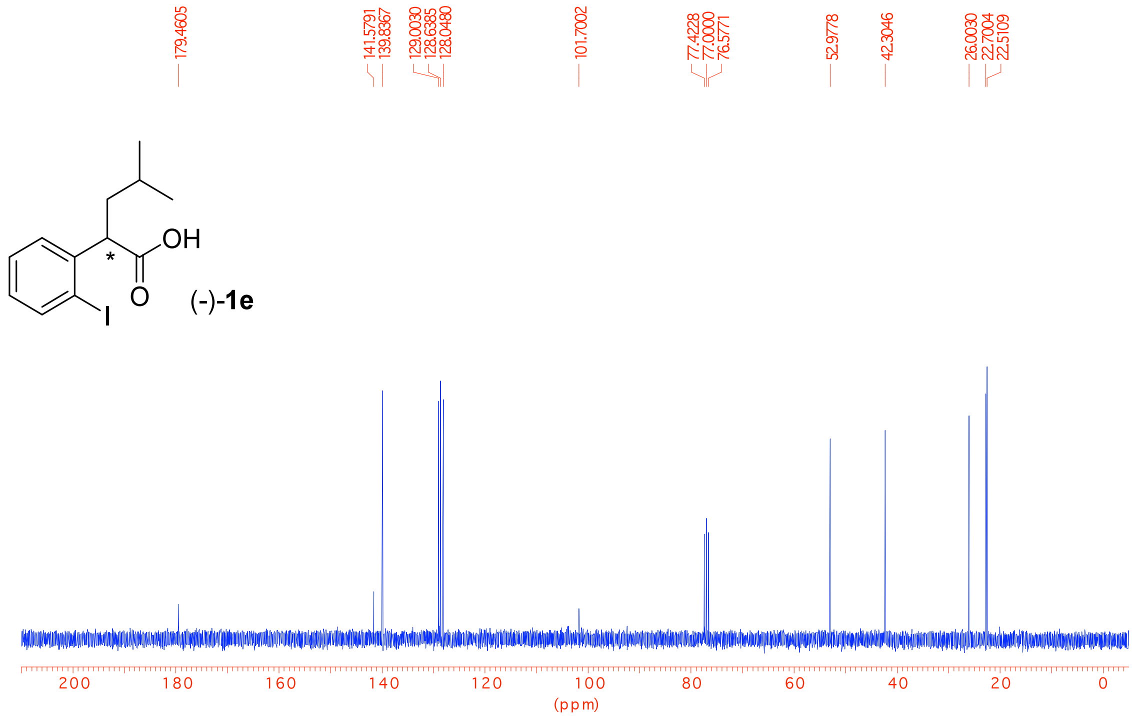
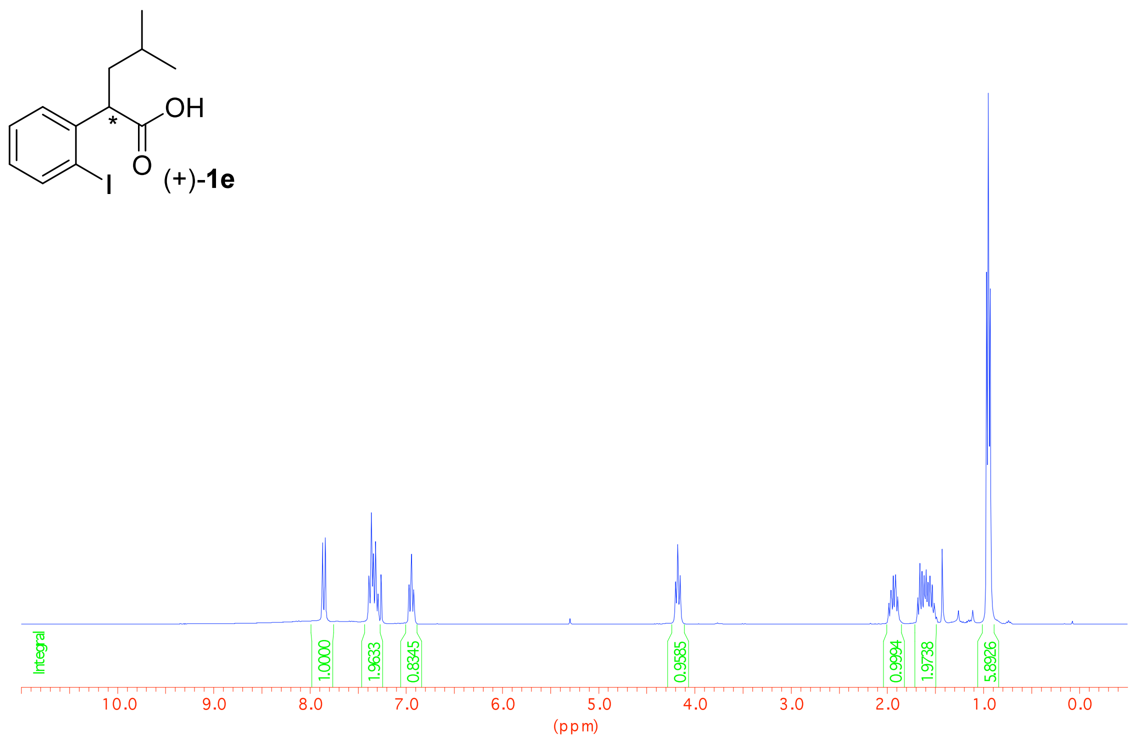


Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13654	2362.69	7.8722	39792848	14.6
2	13659	2361.75	7.8691	42746632	15.7
3	13696	2354.76	7.8458	43312632	15.9
4	13701	2353.82	7.8427	45714456	16.7
5	14413	2219.36	7.3947	21968648	8.0
6	14423	2217.47	7.3884	28523132	10.4
7	14455	2211.43	7.3682	63223800	23.1
8	14465	2209.54	7.3619	63724708	23.3
9	14490	2204.82	7.3462	37193080	13.6
10	14495	2203.87	7.3431	38365016	14.0
11	14533	2196.70	7.3191	46988296	17.2
12	14569	2189.90	7.2965	16560941	6.1
13	14574	2188.95	7.2933	17178052	6.3
14	14627	2178.94	7.2600	42240384	15.5
15	15077	2093.96	6.9769	24242742	8.9
16	15088	2091.89	6.9699	24947520	9.1
17	15119	2086.03	6.9504	34793432	12.7
18	15125	2084.90	6.9467	34787800	12.7
19	15129	2084.14	6.9441	32602468	11.9
20	15157	2078.86	6.9265	21142742	7.7
21	15167	2076.97	6.9202	21573776	7.9
22	19482	1262.09	4.2052	28765580	10.5
23	19523	1254.35	4.1794	45884092	16.8
24	19561	1247.18	4.1555	34817952	12.7
25	23008	596.22	1.9865	14807532	5.4
26	23043	589.61	1.9645	21090250	7.7
27	23079	582.81	1.9419	26841592	9.8
28	23085	581.68	1.9381	25826108	9.5
29	23114	576.20	1.9199	26022428	9.5
30	23121	574.88	1.9154	27348804	10.0
31	23156	568.27	1.8934	17366266	6.4
32	23485	506.14	1.6864	18744898	6.9
33	23523	498.97	1.6625	43235136	15.8
34	23559	492.17	1.6398	34323764	12.6
35	23594	485.56	1.6178	30642594	11.2
36	23608	482.91	1.6090	9965807	3.6
37	23628	479.14	1.5964	29979736	11.0
38	23657	473.66	1.5782	26138486	9.6
39	23692	467.05	1.5562	30332416	11.1
40	23727	460.44	1.5341	24659732	9.0
41	23762	453.83	1.5121	12906752	4.7
42	23797	447.22	1.4901	4087304	1.5
43	24626	290.67	0.9685	247734208	90.7
44	24652	285.76	0.9521	269545120	98.7
45	24659	284.44	0.9477	273111808	100.0
46	24685	279.53	0.9314	222444080	81.4

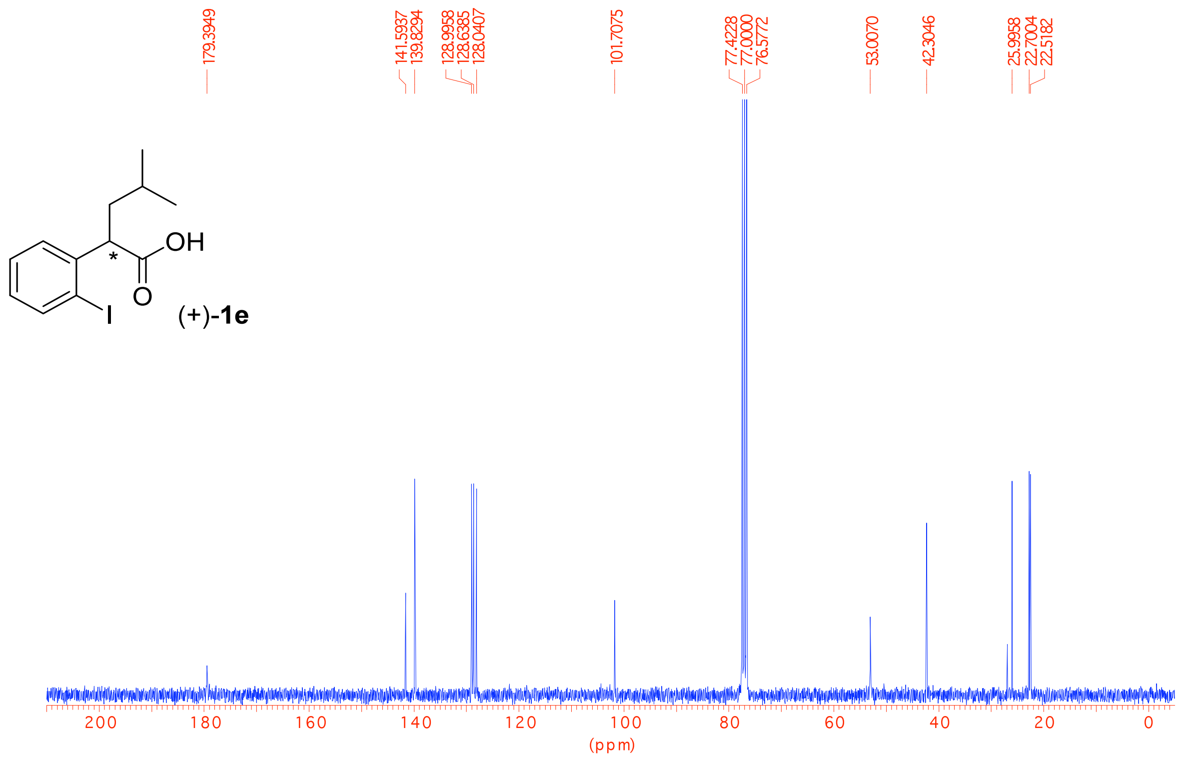


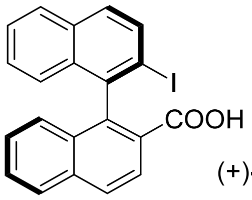


Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13621	2360.99	7.8666	56855952	15.3
2	13663	2353.06	7.8401	60514580	16.3
3	14386	2216.52	7.3852	33708180	9.1

4	14423	2209.54	7.3619	78008584	21.0
5	14459	2202.74	7.3393	49389912	13.3
6	14496	2195.75	7.3160	57641200	15.5
7	14537	2188.01	7.2902	21217280	5.7
8	14585	2178.94	7.2600	34719984	9.3
9	14589	2178.19	7.2575	33182424	8.9
10	15045	2092.07	6.9706	27327660	7.4
11	15049	2091.32	6.9680	27618178	7.4
12	15086	2084.33	6.9448	48965036	13.2
13	15124	2077.16	6.9209	24001132	6.5
14	19447	1260.77	4.2008	29541244	8.0
15	19485	1253.60	4.1768	55852120	15.0
16	19525	1246.04	4.1517	33927056	9.1
17	22973	594.90	1.9821	14762222	4.0
18	23010	587.91	1.9589	23678732	6.4
19	23046	581.11	1.9362	33768476	9.1
20	23082	574.32	1.9136	34717932	9.3
21	23119	567.33	1.8903	19204160	5.2
22	23449	505.01	1.6826	18627924	5.0
23	23486	498.02	1.6594	42606888	11.5
24	23522	491.22	1.6367	36864296	9.9
25	23556	484.80	1.6153	34163800	9.2
26	23590	478.38	1.5939	38020664	10.2
27	23620	472.72	1.5750	29388012	7.9
28	23654	466.30	1.5536	33743792	9.1
29	23689	459.69	1.5316	27594420	7.4
30	23724	453.08	1.5096	14829555	4.0
31	23759	446.47	1.4876	5095060	1.4
32	24588	289.91	0.9660	246145728	66.3
33	24617	284.44	0.9477	371386304	100.0
34	24646	278.96	0.9295	234430928	63.1





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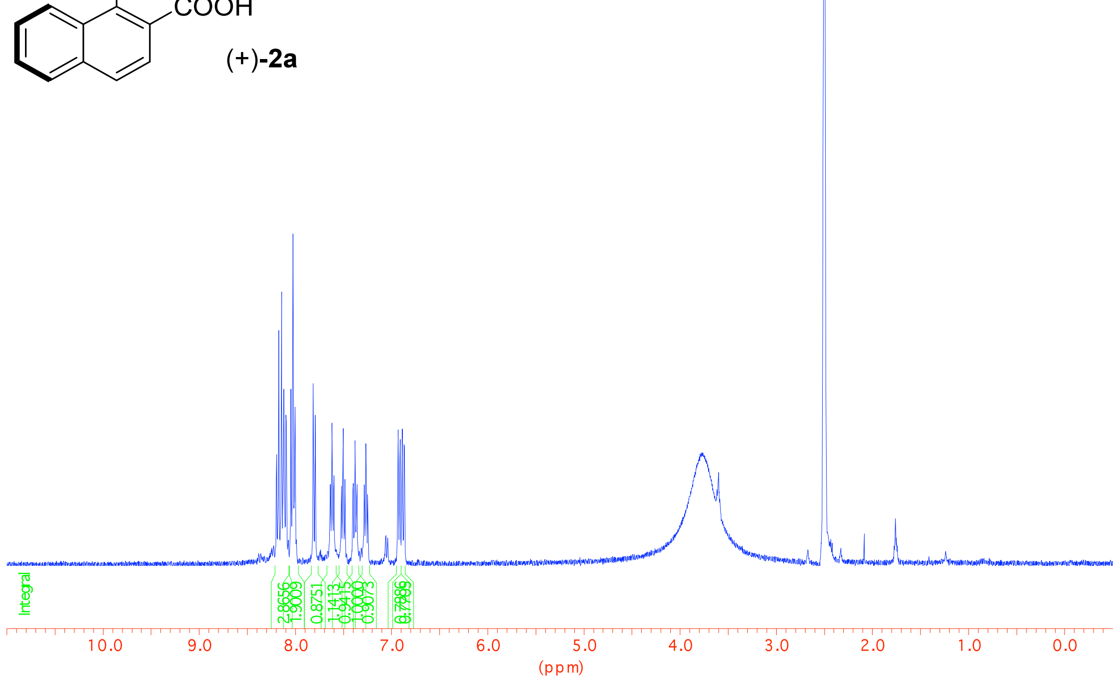
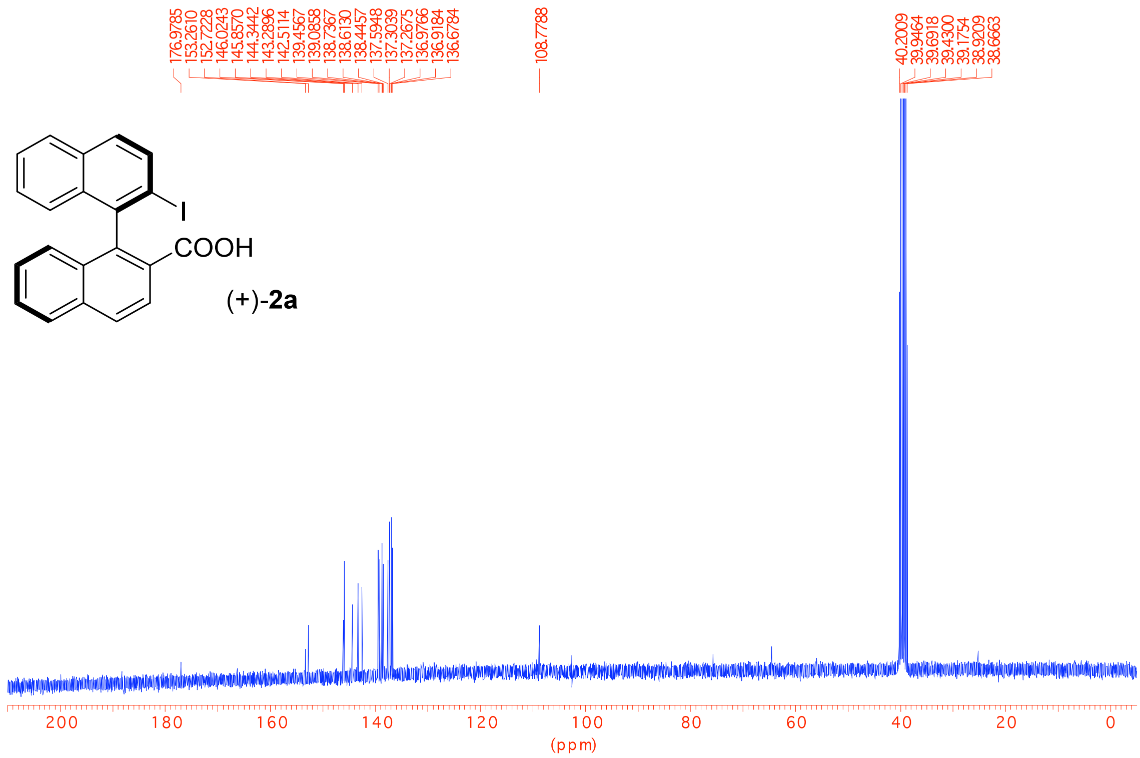
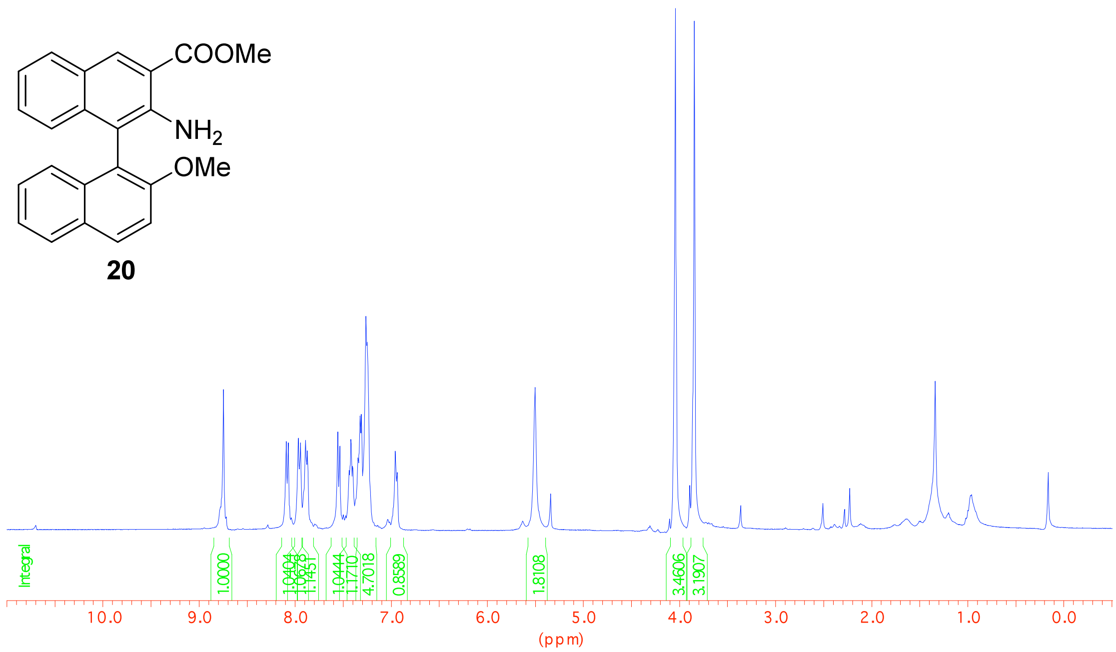


Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	11219	3278.38	8.1933	29486550	6.0
2	11254	3269.83	8.1719	63884896	13.0
3	11303	3257.84	8.1420	74651360	15.2
4	11339	3249.04	8.1200	47630520	9.7
5	11379	3239.26	8.0955	40453176	8.2
6	11465	3218.23	8.0430	47694540	9.7
7	11501	3209.43	8.0210	90589160	18.4
8	11530	3202.33	8.0032	42700732	8.7
9	11842	3126.04	7.8126	49159240	10.0
10	11877	3117.48	7.7912	40462668	8.2
11	12134	3054.64	7.6341	21240756	4.3
12	12163	3047.55	7.6164	38273884	7.8
13	12196	3039.48	7.5962	23676298	4.8
14	12321	3008.91	7.5198	20842558	4.2
15	12350	3001.82	7.5021	36696260	7.5
16	12378	2994.97	7.4850	22737464	4.6
17	12523	2959.51	7.3964	21521680	4.4
18	12553	2952.18	7.3780	33407662	6.8
19	12586	2944.11	7.3579	21349636	4.3
20	12710	2913.79	7.2821	21143538	4.3
21	12740	2906.45	7.2638	32544276	6.6
22	12769	2899.36	7.2460	18497054	3.8
23	13283	2773.67	6.9319	36369504	7.4
24	13319	2764.87	6.9099	33703132	6.8
25	13355	2756.06	6.8879	36669424	7.4
26	13389	2747.75	6.8671	32352782	6.6
27	20528	1002.04	2.5043	383828640	78.0

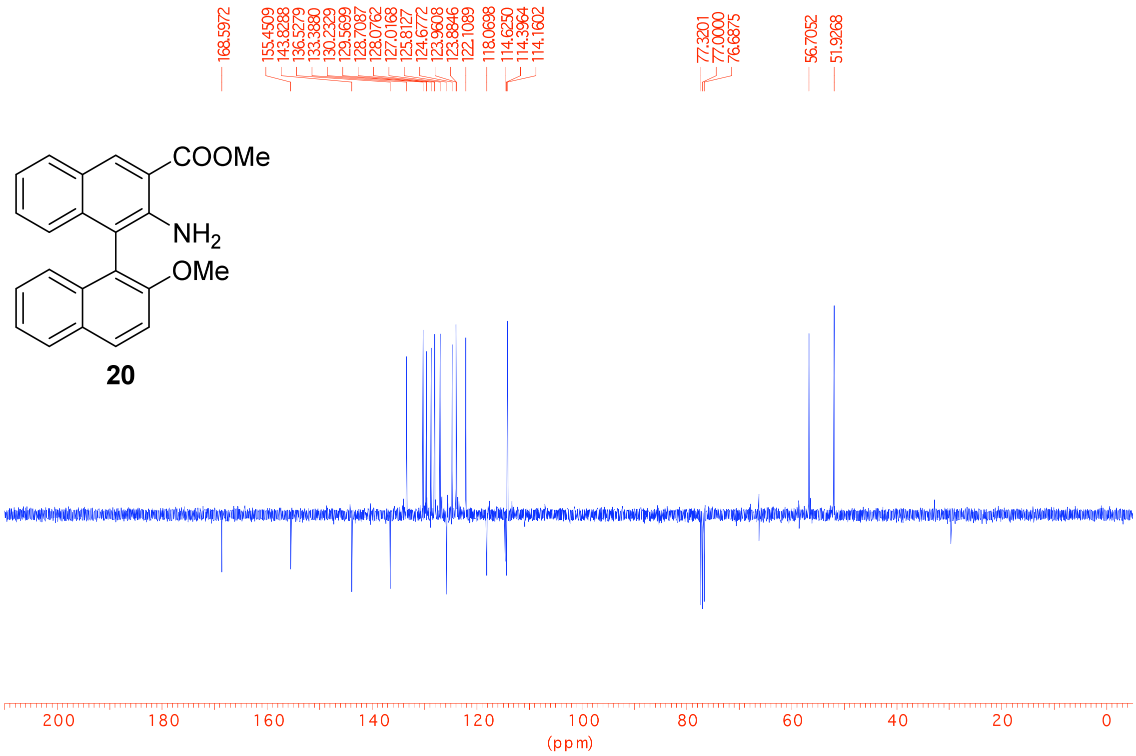
28	20535	1000.32	2.5000	492327840	100.0
29	20541	998.86	2.4963	396162208	80.5

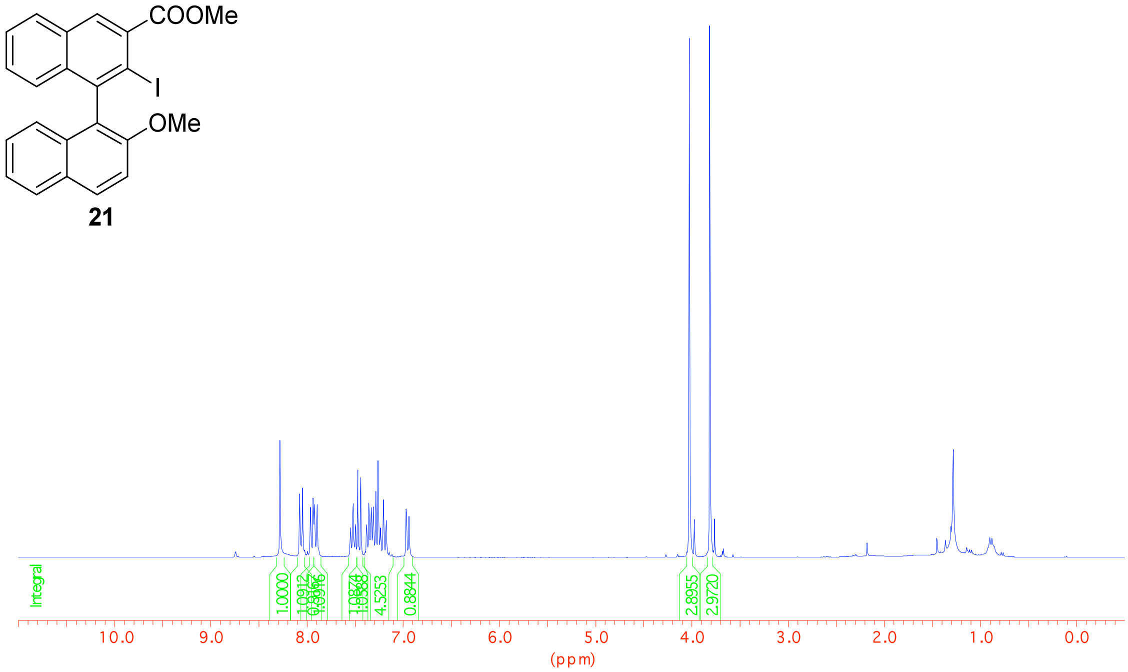




Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	10334	3498.42	8.7432	86358968	26.6
2	11401	3237.51	8.0911	53899652	16.6
3	11438	3228.46	8.0685	53076616	16.4
4	11610	3186.40	7.9634	56016132	17.3
5	11643	3178.33	7.9432	53040332	16.3
6	11731	3156.81	7.8895	54586920	16.8
7	11760	3149.72	7.8717	48038932	14.8
8	12281	3022.32	7.5533	59952156	18.5
9	12317	3013.52	7.5313	50997920	15.7
10	12475	2974.88	7.4348	35879452	11.1
11	12502	2968.28	7.4183	55306956	17.0
12	12533	2960.70	7.3993	38552772	11.9
13	12626	2937.96	7.3425	43701656	13.5
14	12658	2930.13	7.3229	69817336	21.5
15	12681	2924.51	7.3089	70962552	21.9
16	12761	2904.94	7.2600	132148488	40.7
17	12780	2900.30	7.2484	115865992	35.7
18	13259	2783.17	6.9557	47952584	14.8
19	13290	2775.59	6.9367	34473428	10.6
20	15638	2201.43	5.5018	87552568	27.0
21	18032	1616.02	4.0387	324526464	100.0
22	18351	1538.01	3.8438	316856416	97.6





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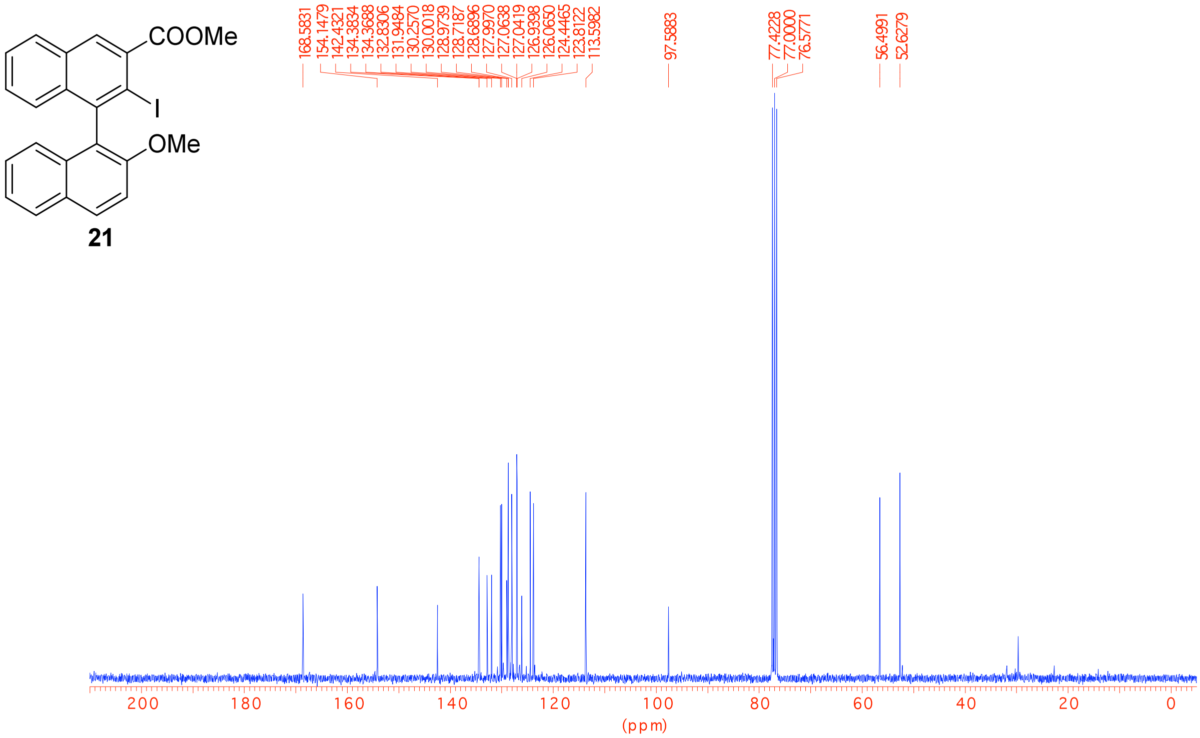
Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13009	2484.50	8.2781	72529856	21.9
2	13332	2423.50	8.0748	39424988	11.9
3	13380	2414.44	8.0446	43168564	13.1
4	13513	2389.32	7.9609	31134270	9.4
5	13556	2381.20	7.9339	36794900	11.1
6	13577	2377.23	7.9207	32723872	9.9
7	13620	2369.11	7.8936	32809292	9.9
8	14172	2264.87	7.5463	15889497	4.8
9	14177	2263.92	7.5431	18296918	5.5
10	14214	2256.94	7.5199	33573016	10.2
11	14251	2249.95	7.4966	18949250	5.7
12	14257	2248.82	7.4928	20389008	6.2
13	14292	2242.21	7.4708	54409768	16.5
14	14340	2233.14	7.4406	49543936	15.0
15	14435	2215.20	7.3808	16615229	5.0
16	14441	2214.07	7.3770	20210206	6.1
17	14471	2208.40	7.3582	24128256	7.3
18	14477	2207.27	7.3544	33731180	10.2
19	14503	2202.36	7.3380	20516162	6.2
20	14513	2200.47	7.3317	30831430	9.3
21	14519	2199.34	7.3280	27105636	8.2
22	14539	2195.56	7.3154	18392116	5.6
23	14547	2194.05	7.3103	31387172	9.5
24	14554	2192.73	7.3059	29133836	8.8
25	14584	2187.06	7.2871	37014408	11.2
26	14591	2185.74	7.2827	41083640	12.4
27	14627	2178.94	7.2600	60101500	18.2
28	14635	2177.43	7.2550	34207376	10.3
29	14665	2171.77	7.2361	18315900	5.5
30	14672	2170.45	7.2317	17544804	5.3
31	14719	2161.57	7.2021	35917668	10.9

32	14764	2153.07	7.1738	22678576	6.9
33	15093	2090.94	6.9668	29950204	9.1
34	15137	2082.63	6.9391	25504416	7.7
35	19770	1207.71	4.0239	322599904	97.6
36	20104	1144.63	3.8138	330524064	100.0



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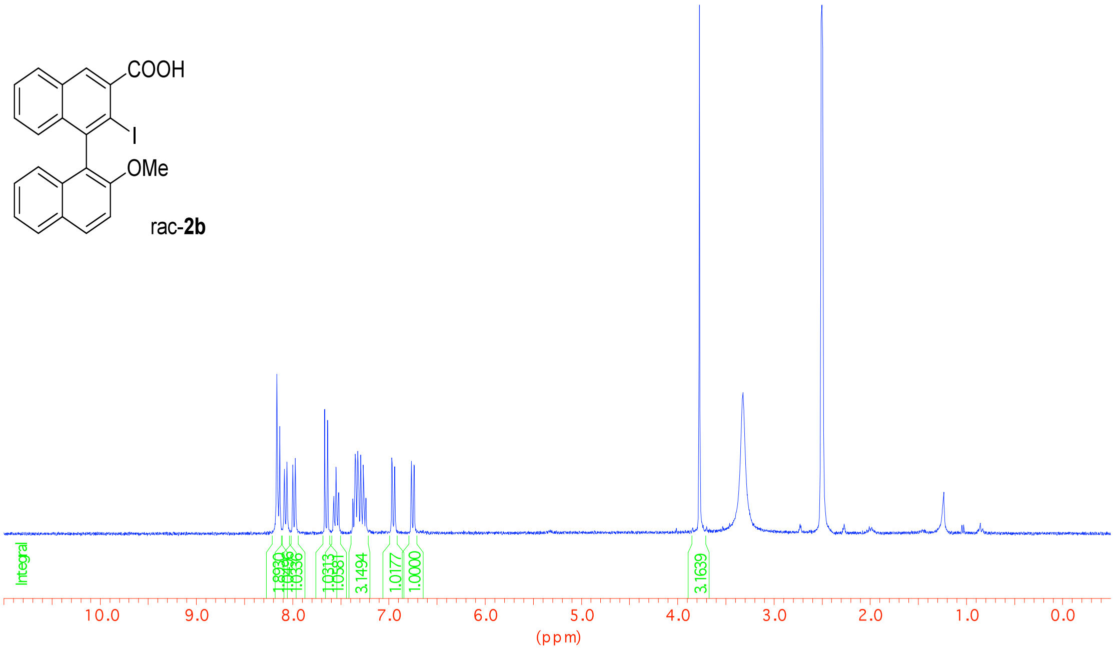
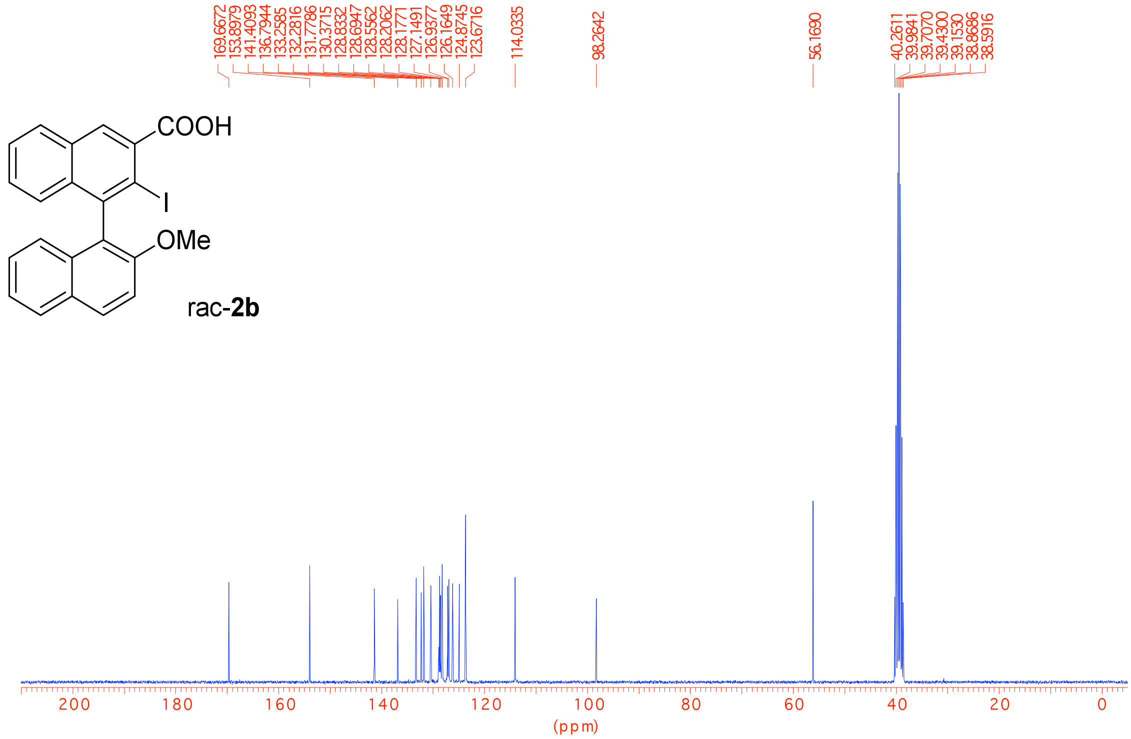


Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13218	2450.13	8.1636	49991820	15.2
2	13265	2441.26	8.1340	33780836	10.2
3	13343	2426.53	8.0849	20446832	6.2
4	13386	2418.41	8.0579	22646104	6.9
5	13485	2399.71	7.9956	21712632	6.6
6	13527	2391.78	7.9691	23862166	7.2
7	14010	2300.57	7.6652	39084960	11.8
8	14059	2291.31	7.6344	35697060	10.8
9	14162	2271.86	7.5696	12034087	3.6
10	14199	2264.87	7.5463	21112914	6.4
11	14237	2257.70	7.5224	13116206	4.0
12	14476	2212.56	7.3720	11229806	3.4
13	14513	2205.58	7.3487	25124272	7.6
14	14520	2204.25	7.3443	22959412	7.0
15	14556	2197.45	7.3217	26040168	7.9
16	14564	2195.94	7.3166	21522992	6.5
17	14605	2188.20	7.2908	24852640	7.5
18	14609	2187.45	7.2883	24400840	7.4
19	14649	2179.89	7.2632	21773680	6.6
20	14656	2178.57	7.2588	18775596	5.7
21	14685	2173.09	7.2405	11442852	3.5
22	14692	2171.77	7.2361	11358924	3.4
23	15120	2090.95	6.9668	24003654	7.3
24	15165	2082.45	6.9385	21176612	6.4
25	15441	2030.33	6.7648	22899948	6.9
26	15485	2022.02	6.7371	21695972	6.6
27	20195	1132.55	3.7735	227920928	69.1
28	20915	996.58	3.3205	44344420	13.4
29	22209	752.21	2.5063	235623632	71.4
30	22219	750.32	2.5000	329870272	100.0
31	22228	748.63	2.4943	249817664	75.7



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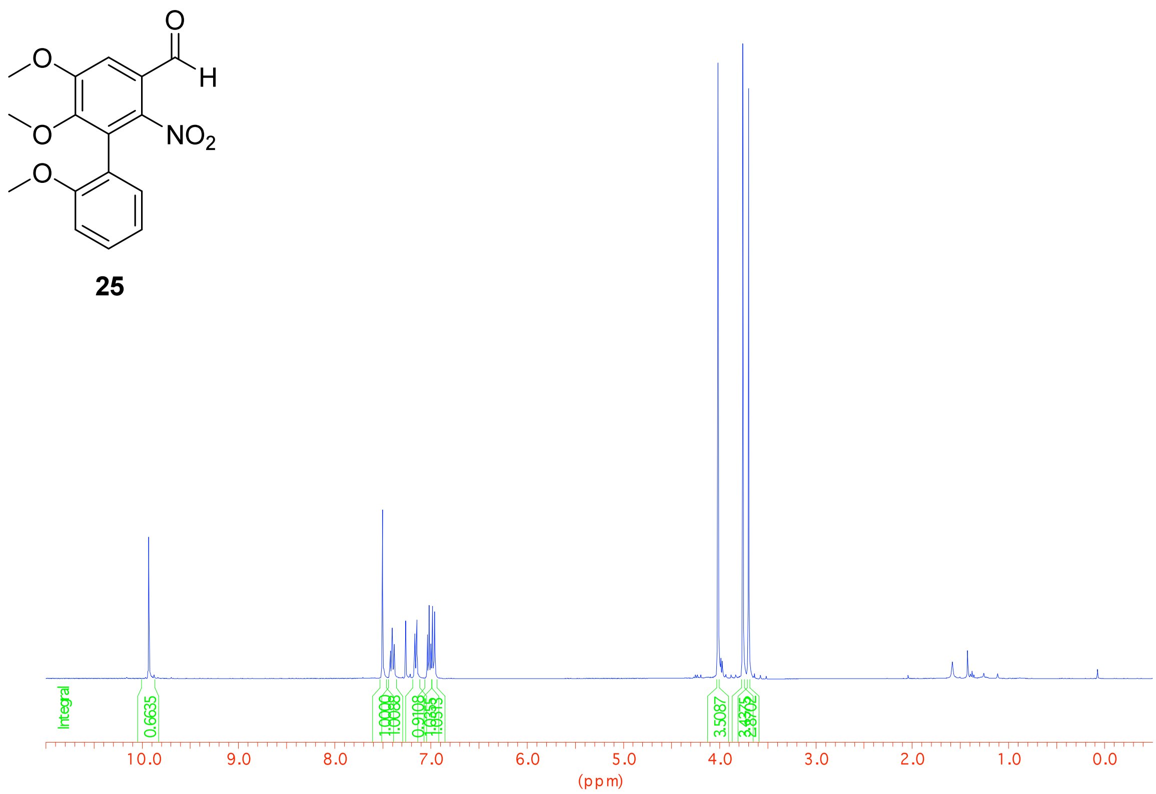

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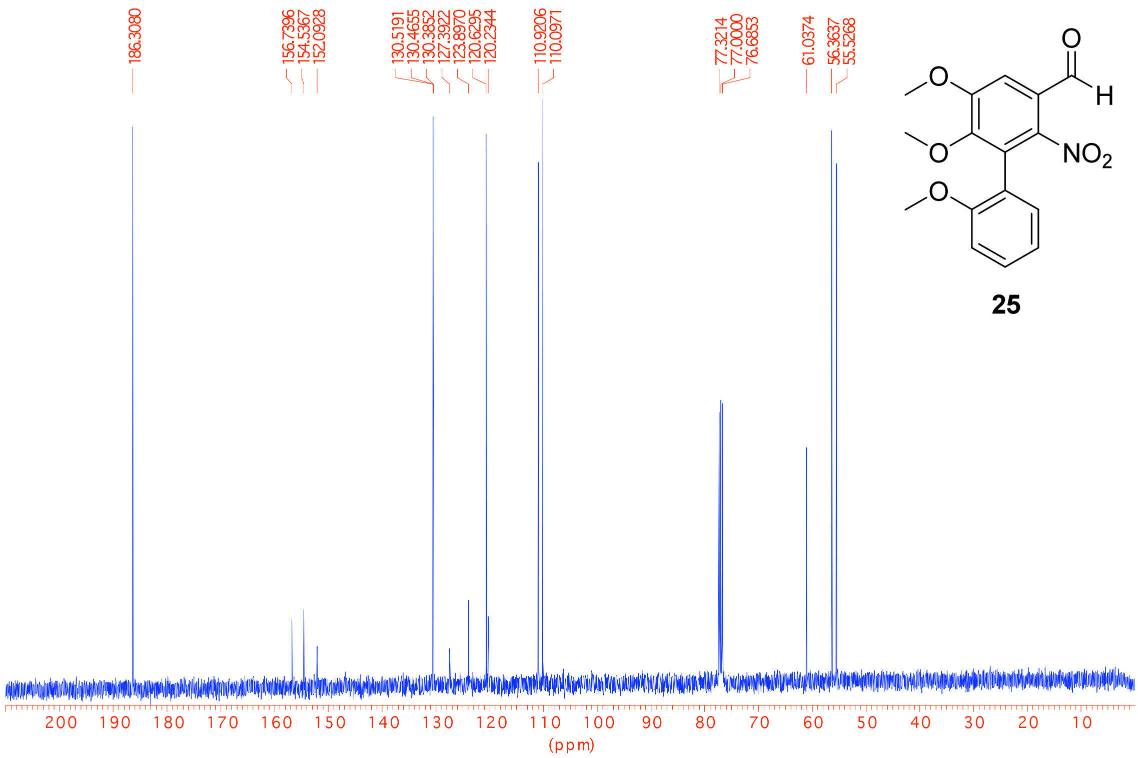
Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13152	3973.30	9.9300	92834688	22.1
2	17127	3001.29	7.5008	110945232	26.5
3	17253	2970.48	7.4238	14745532	3.5
4	17260	2968.77	7.4195	17427192	4.2
5	17290	2961.43	7.4012	32655570	7.8
6	17318	2954.58	7.3841	19712016	4.7
7	17324	2953.12	7.3804	22048652	5.3
8	17521	2904.94	7.2600	37446784	8.9
9	17672	2868.02	7.1677	24901836	5.9
10	17679	2866.31	7.1634	28863352	6.9
11	17703	2860.44	7.1488	35746992	8.5
12	17709	2858.97	7.1451	37954876	9.0
13	17888	2815.20	7.0357	28351168	6.8
14	17918	2807.86	7.0174	47692676	11.4
15	17949	2800.28	6.9984	22119764	5.3
16	17976	2793.68	6.9819	47159936	11.2
17	18010	2785.37	6.9612	43486436	10.4
18	22830	1606.72	4.0155	406389664	96.9
19	23253	1503.29	3.7570	419398880	100.0
20	23347	1480.30	3.6996	389471456	92.9



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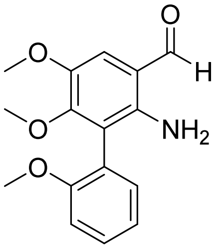

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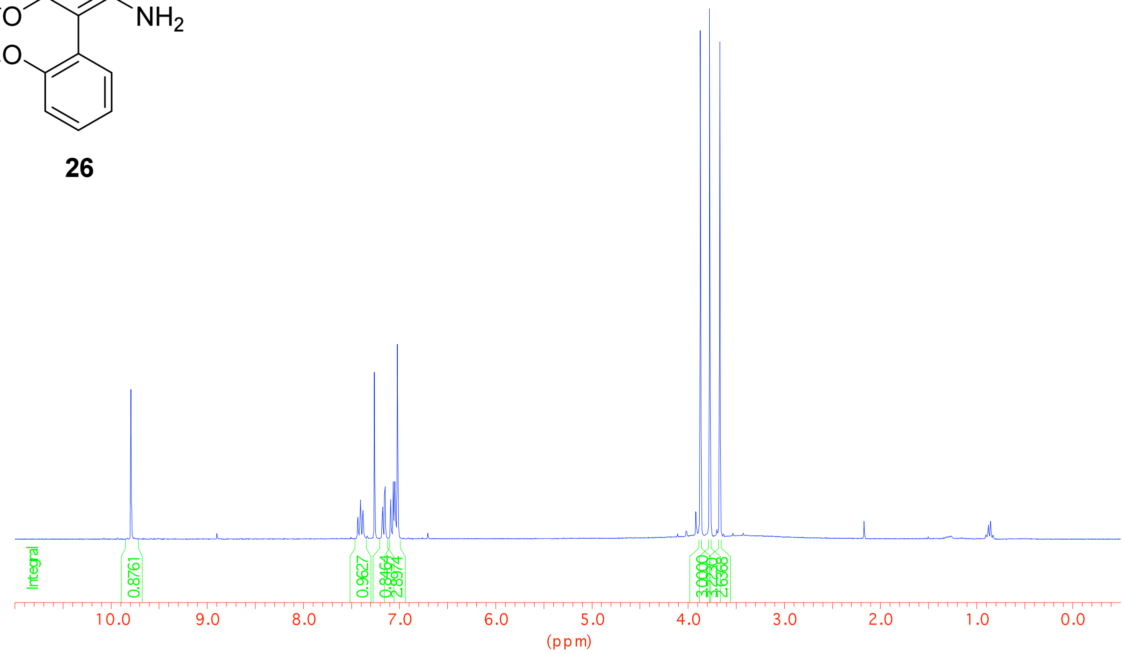
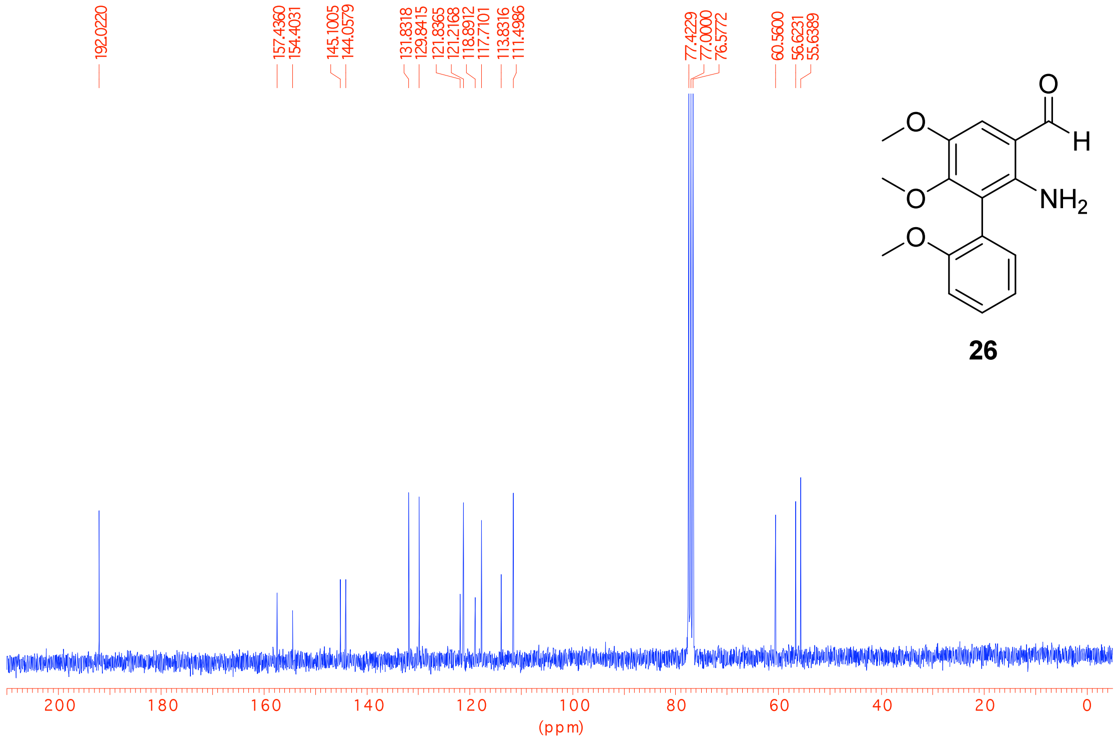


Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	5956	2938.87	9.7920	89900872	28.2
2	9699	2232.02	7.4368	10090988	3.2
3	9709	2230.13	7.4305	13117066	4.1
4	9743	2223.71	7.4091	19778170	6.2
5	9748	2222.76	7.4060	23394138	7.3
6	9752	2222.01	7.4035	22659848	7.1
7	9782	2216.34	7.3846	13658481	4.3
8	9792	2214.45	7.3783	17305800	5.4
9	9980	2178.95	7.2600	100295544	31.5
10	10108	2154.78	7.1795	14216381	4.5
11	10117	2153.08	7.1738	19197140	6.0
12	10147	2147.41	7.1549	26444484	8.3
13	10156	2145.71	7.1493	31445832	9.9
14	10246	2128.72	7.0926	18423736	5.8
15	10251	2127.77	7.0895	23801926	7.5
16	10285	2121.35	7.0681	26225662	8.2
17	10290	2120.41	7.0649	34509036	10.8
18	10316	2115.50	7.0486	34539216	10.8
19	10323	2114.18	7.0442	26280524	8.2
20	10329	2113.04	7.0404	21302014	6.7
21	10357	2107.76	7.0228	117054824	36.7
22	15365	1162.01	3.8717	305395552	95.9
23	15520	1132.74	3.7742	318599840	100.0
24	15687	1101.20	3.6691	298529280	93.7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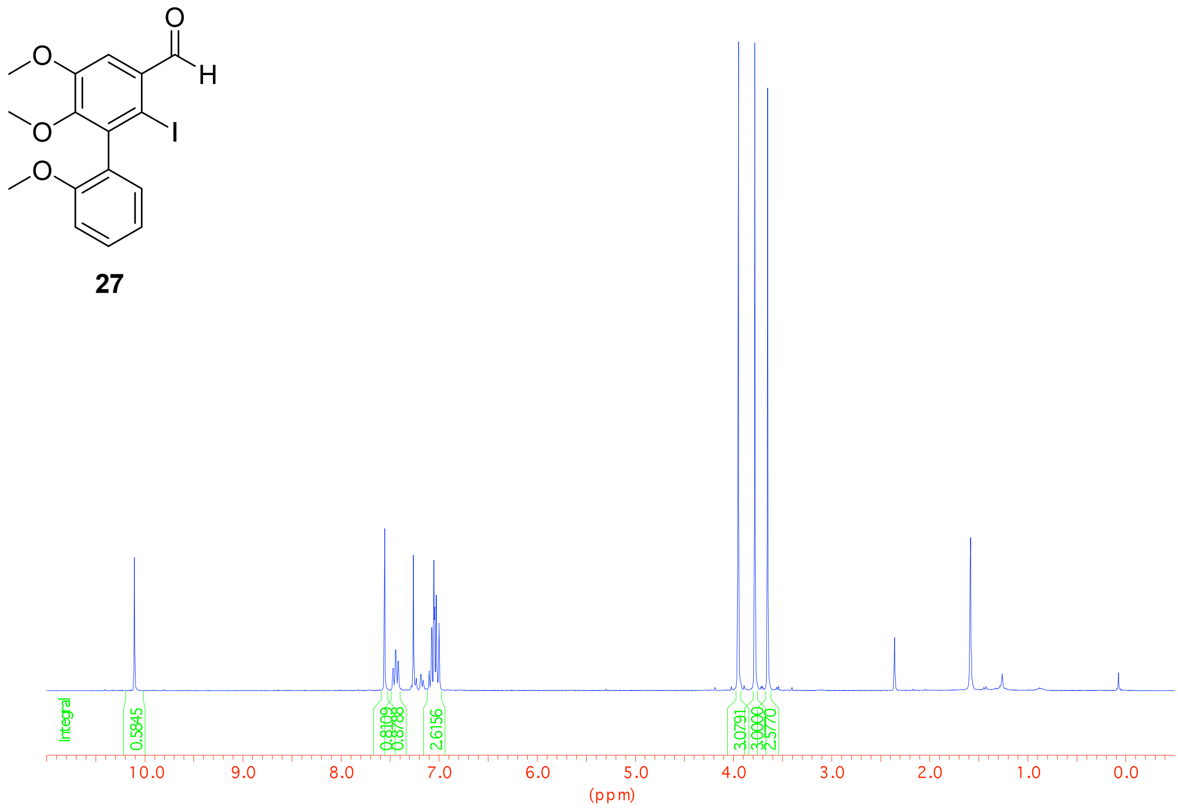
154.4031
145.1005
144.0579
131.8318
129.8415
121.8365
121.2168
118.8912
117.7101
113.8316
111.4986
77.4229
77.0000
76.5772
60.5600
56.6231
55.6389
O
H
O
O
NH2
O
200
180
160
140
120
100
80
60
40
20
0
(ppm)

26


O
O
H
O
I
O
Integral
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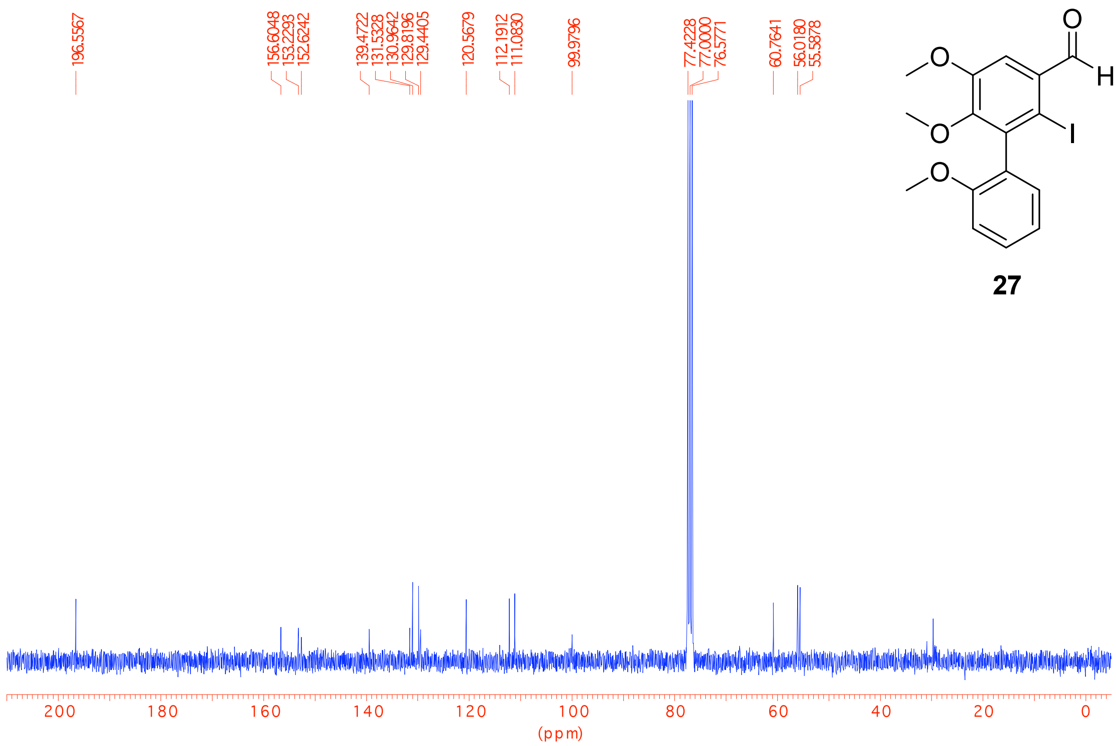
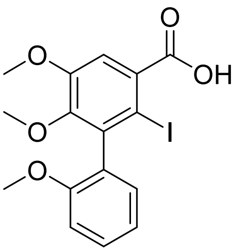
0.8788
2.6156
3.0791
3.0000
2.5770
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

27

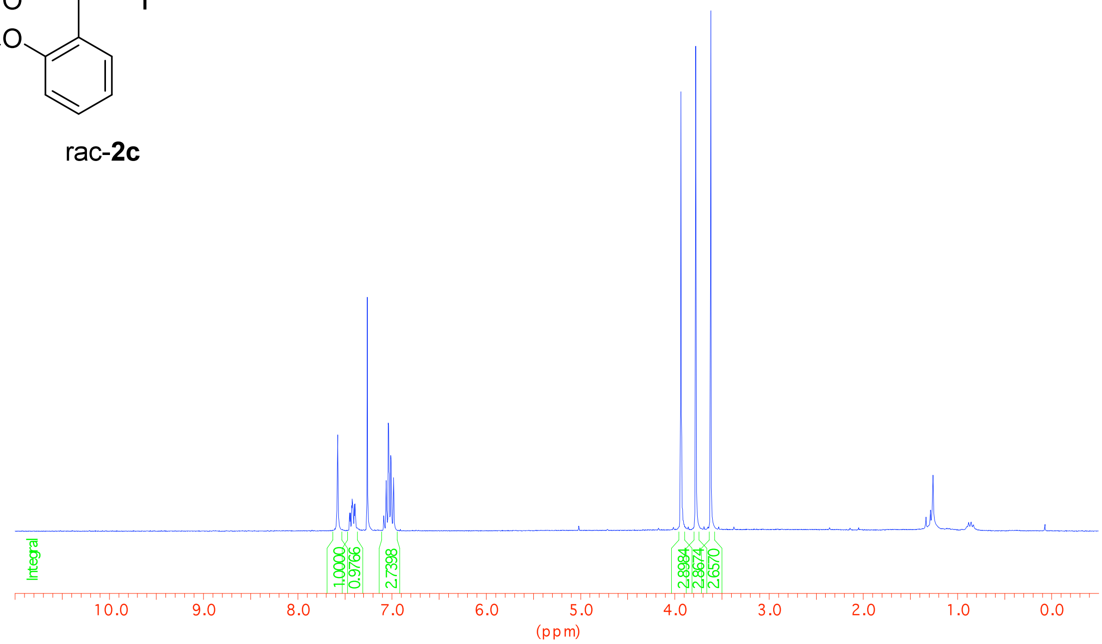
Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	10107	3032.72	10.1047	62308228	19.9
2	14162	2266.95	7.5532	76378416	24.3
3	14296	2241.64	7.4689	10301807	3.3
4	14309	2239.19	7.4607	11020817	3.5
5	14333	2234.65	7.4456	13763003	4.4
6	14344	2232.58	7.4387	18682352	6.0
7	14352	2231.07	7.4337	15340009	4.9
8	14376	2226.53	7.4186	14214494	4.5
9	14389	2224.08	7.4104	14810664	4.7
10	14628	2178.94	7.2600	159934208	51.0
11	14888	2129.84	7.0964	9577741	3.1
12	14928	2122.29	7.0712	29025248	9.3
13	14962	2115.87	7.0498	56858640	18.1
14	14973	2113.79	7.0429	40510992	12.9
15	15000	2108.69	7.0259	44533424	14.2
16	15044	2100.38	6.9982	31329540	10.0
17	19892	1184.86	3.9478	313685920	100.0
18	20157	1134.81	3.7811	311913408	99.4
19	20368	1094.97	3.6483	290644416	92.7



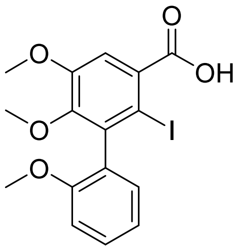


rac-**2c**

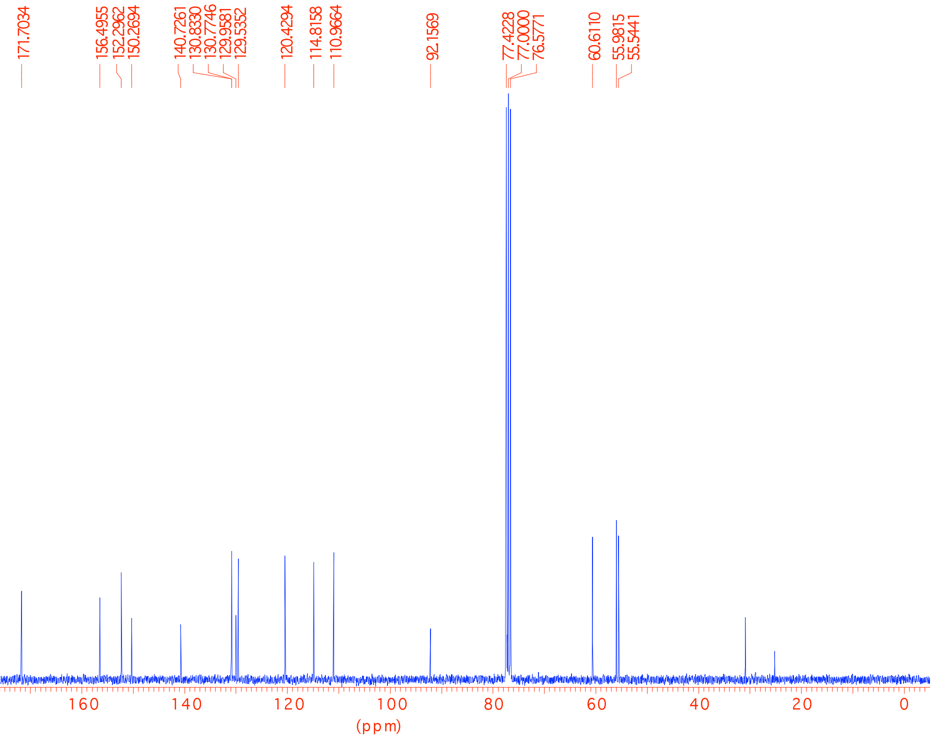


Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14128	2273.56	7.5752	93457096	18.5
2	14366	2228.61	7.4255	25190896	5.0
3	14374	2227.10	7.4204	31442110	6.2
4	14378	2226.34	7.4179	30829598	6.1
5	14386	2224.83	7.4129	24287924	4.8
6	14410	2220.30	7.3978	26117260	5.2
7	14422	2218.03	7.3902	26515672	5.3
8	14629	2178.94	7.2600	226573920	44.9
9	14948	2118.70	7.0593	49302676	9.8
10	14952	2117.95	7.0568	46262652	9.2
11	14984	2111.90	7.0366	105161664	20.9
12	14996	2109.64	7.0291	70041712	13.9
13	15025	2104.16	7.0108	73472864	14.6
14	15071	2095.47	6.9819	51992584	10.3
15	19919	1179.95	3.9315	425630240	84.4
16	20166	1133.30	3.7760	469932128	93.2
17	20420	1085.33	3.6162	504285280	100.0



rac-**2c**



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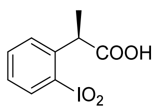
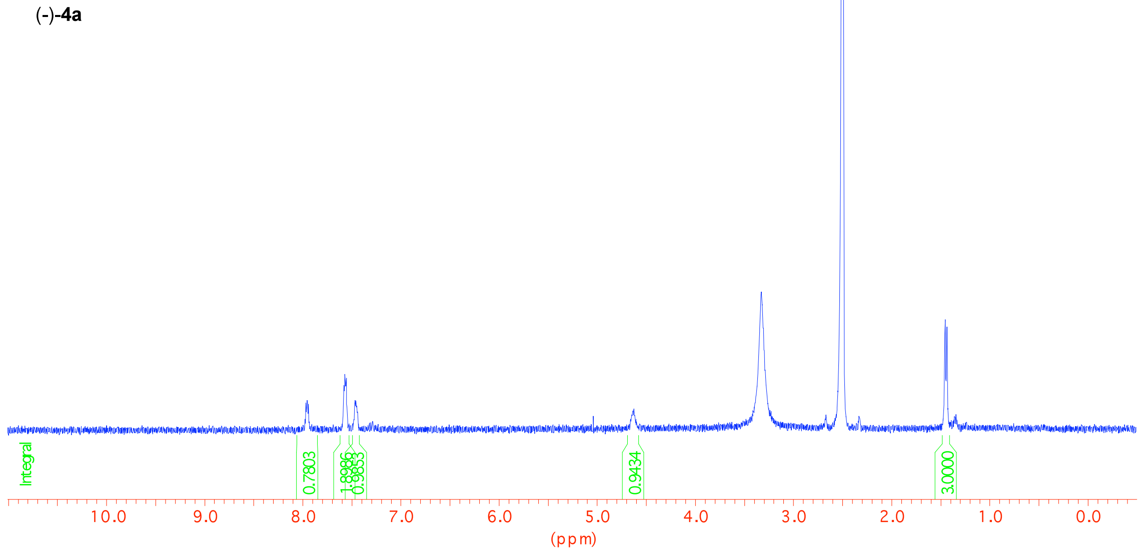
156.4955
152.2962
150.2694
140.7261
130.8330
130.7746
129.9581
129.5332
120.4294
114.8158
110.9664
92.1569
77.4228
77.0000
76.5771
60.6110
55.9815
55.5441
200
180
160
140
120
100
80
60
40
20
0
(ppm)



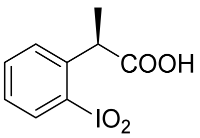
(-)-**4a**



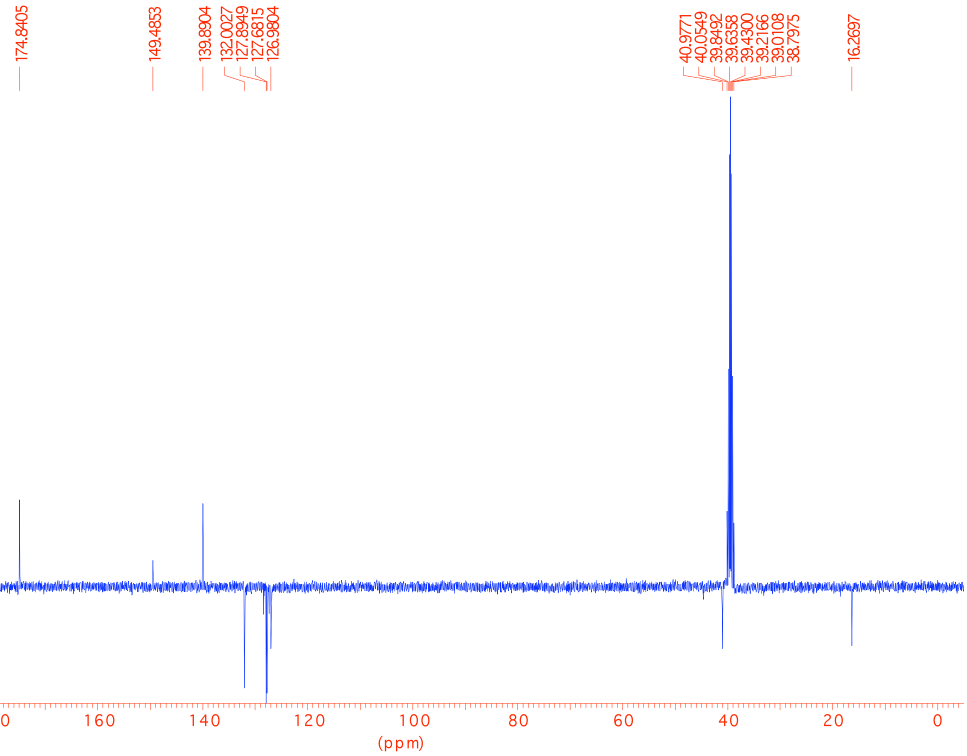
Integral
0.7803
1.8986
0.9853
0.9434
3.0000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

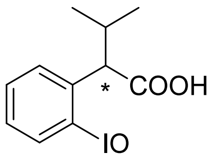
Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	11593	3187.17	7.9653	7242325	1.8
2	11609	3183.26	7.9556	7955366	2.0
3	11616	3181.55	7.9513	7146546	1.8
4	11630	3178.13	7.9427	6920249	1.7
5	12228	3031.90	7.5773	14017515	3.5
6	12241	3028.72	7.5693	15297685	3.8
7	12251	3026.27	7.5632	14915885	3.7
8	12264	3023.09	7.5553	14220605	3.6
9	12411	2987.15	7.4654	7972373	2.0
10	17060	1850.32	4.6243	5621171	1.4
11	20536	1000.32	2.5000	398356640	100.0
12	22247	581.93	1.4544	30654514	7.7
13	22275	575.08	1.4372	28673714	7.2

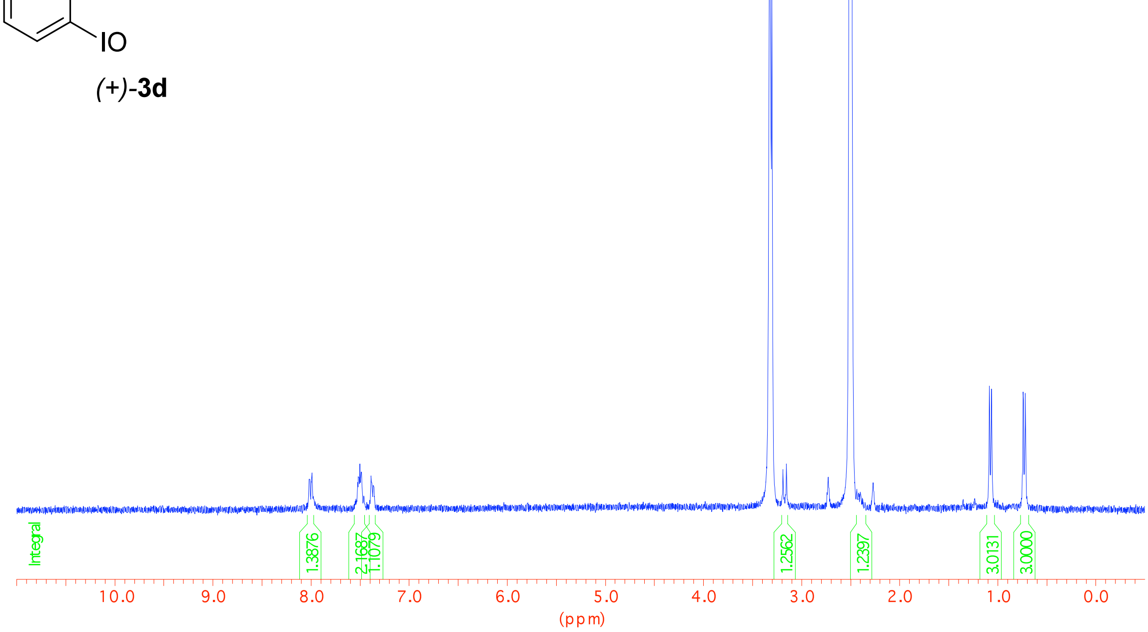


(-)-**4a**



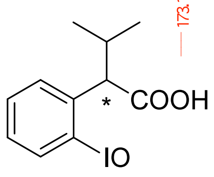


(+)-**3d**

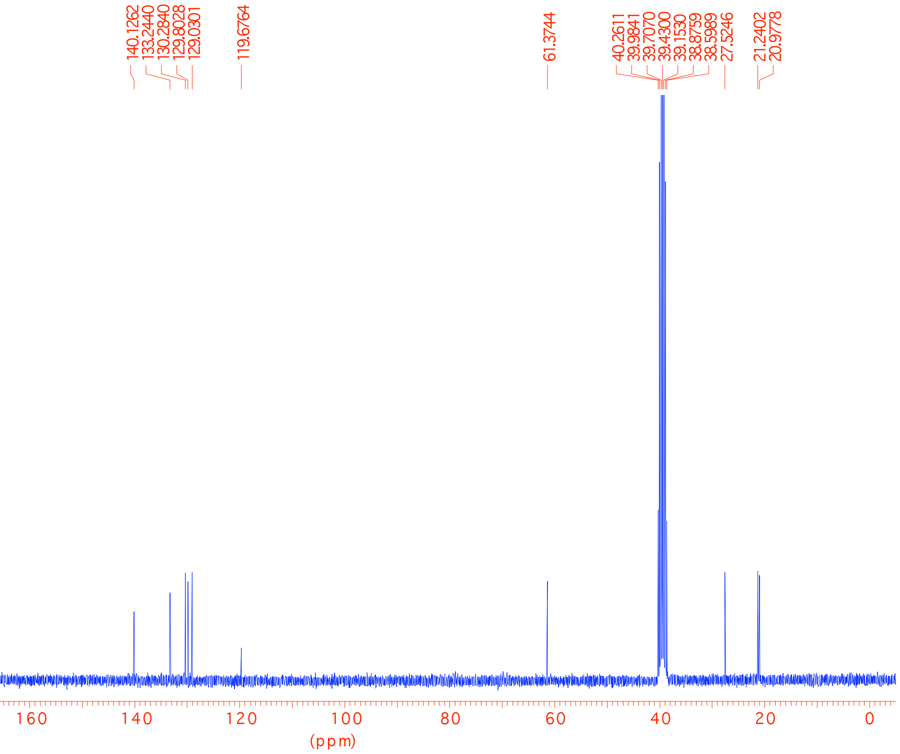


Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13133	2404.43	8.0113	3589870	1.1
2	13171	2397.25	7.9874	4238297	1.3
3	13918	2256.19	7.5174	3855862	1.2
4	13945	2251.09	7.5004	5143749	1.6
5	13971	2246.18	7.4840	4341957	1.4
6	14125	2217.09	7.3871	3923129	1.2
7	14160	2210.49	7.3651	2985353	0.9
8	20798	956.92	3.1884	4574691	1.4
9	20857	945.78	3.1512	5138945	1.6
10	21892	750.32	2.5000	317546016	100.0
11	21999	730.12	2.4327	2586972	0.8
12	22022	725.77	2.4182	2216397	0.7
13	22053	719.92	2.3987	2298685	0.7
14	22124	706.51	2.3540	1263383	0.4
15	24142	325.42	1.0843	13012377	4.1
16	24177	318.81	1.0622	12739238	4.0
17	24691	221.74	0.7388	12436413	3.9
18	24725	215.32	0.7174	12308886	3.9



(+)-**3d**



173.1594
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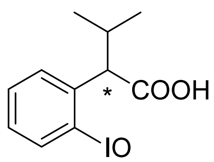
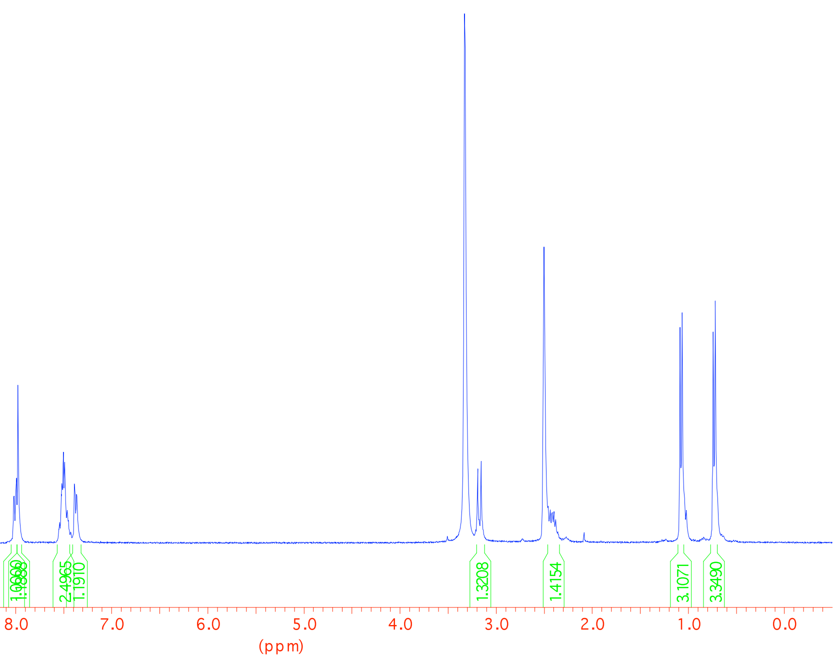
133.2440
130.2840
129.8028
129.0301
119.6764
61.3744
40.2611
39.9841
39.7070
39.4300
39.1530
38.8759
38.5989
27.5246
21.2402
20.9778
(ppm)



(-)-**3d**



Integral
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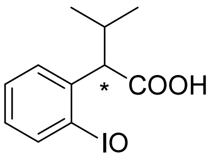
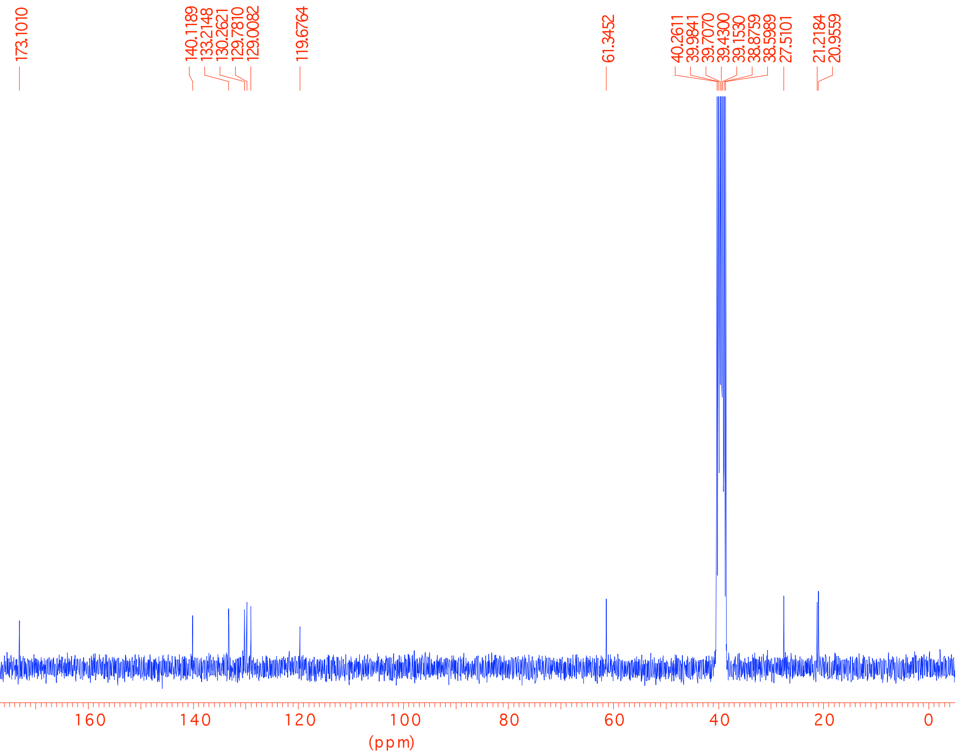
2.4965
1.1910
1.3208
1.4154
3.1071
3.3490
(ppm)

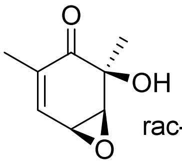
Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13179	2406.70	8.0188	25994358	15.5
2	13189	2404.81	8.0126	26740020	15.9
3	13228	2397.44	7.9880	36849156	22.0
4	13252	2392.91	7.9729	89412920	53.3
5	13938	2263.36	7.5413	11744873	7.0
6	13966	2258.07	7.5237	27696212	16.5
7	13977	2256.00	7.5167	33851612	20.2
8	13987	2254.11	7.5104	34159940	20.4
9	14001	2251.46	7.5016	51618500	30.8
10	14017	2248.44	7.4916	42865024	25.6
11	14025	2246.93	7.4865	45862780	27.3
12	14034	2245.23	7.4809	41967288	25.0
13	14064	2239.57	7.4620	18778008	11.2
14	14181	2217.47	7.3884	33700432	20.1
15	14190	2215.77	7.3827	29767846	17.7
16	14217	2210.67	7.3657	27690288	16.5
17	14228	2208.60	7.3588	26678108	15.9
18	20853	957.49	3.1902	42061848	25.1
19	20911	946.54	3.1538	46312416	27.6
20	21950	750.32	2.5000	167716976	100.0
21	22018	737.48	2.4572	21200944	12.6
22	22054	730.68	2.4346	19037042	11.4
23	22087	724.45	2.4138	17422070	10.4
24	22113	719.54	2.3974	18004276	10.7
25	22145	713.50	2.3773	13477606	8.0
26	24199	325.61	1.0849	122070000	72.8
27	24234	319.00	1.0629	130422880	77.8
28	24747	222.12	0.7401	119667296	71.4
29	24781	215.70	0.7187	137081888	81.7

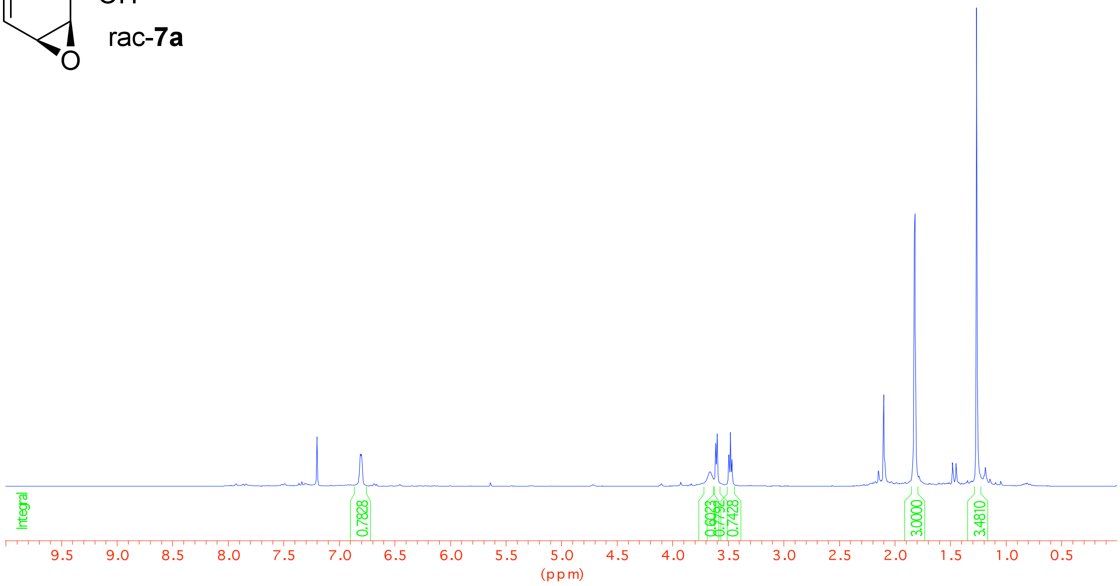


(-)-**3d**



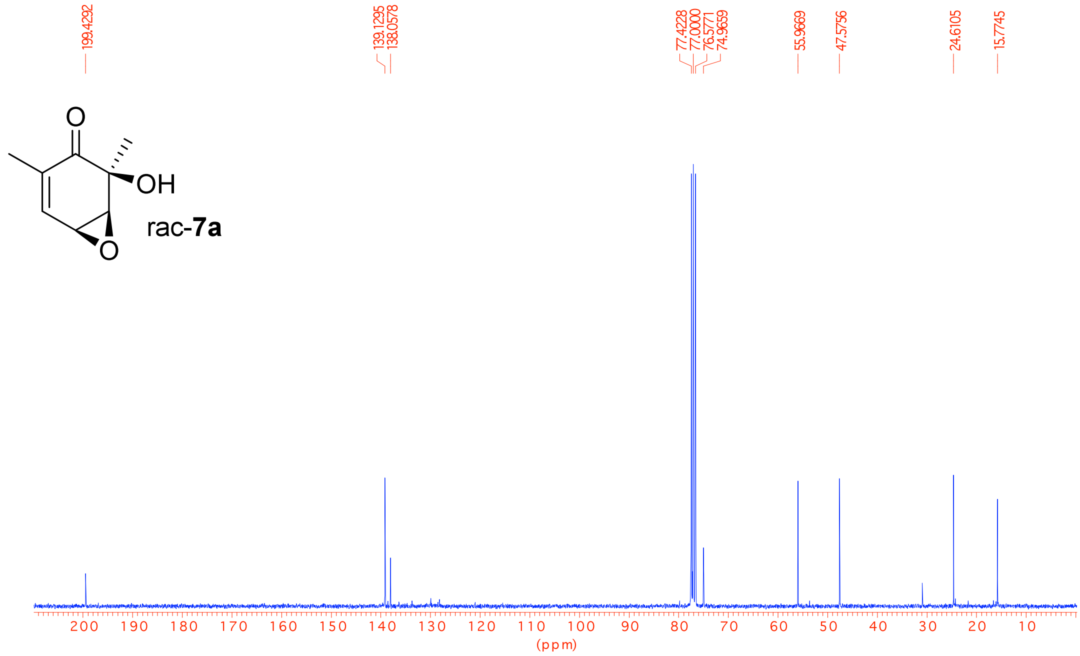


rac-**7a**



Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14521	2178.94	7.2600	47920976	11.1
2	14628	2160.83	7.1996	44467212	10.3
3	15251	2043.18	6.8076	28850444	6.7
4	15261	2041.29	6.8014	28914032	6.7
5	20249	1099.33	3.6628	13164227	3.1
6	20331	1083.84	3.6112	38894560	9.0
7	20352	1079.87	3.5980	47069864	10.9
8	20518	1048.53	3.4936	28318748	6.6
9	20540	1044.37	3.4797	48640912	11.3
10	20561	1040.41	3.4665	24160648	5.6
11	23171	547.52	1.8243	225213360	52.3
12	23179	546.01	1.8192	245246560	57.0
13	24062	379.25	1.2636	430373824	100.0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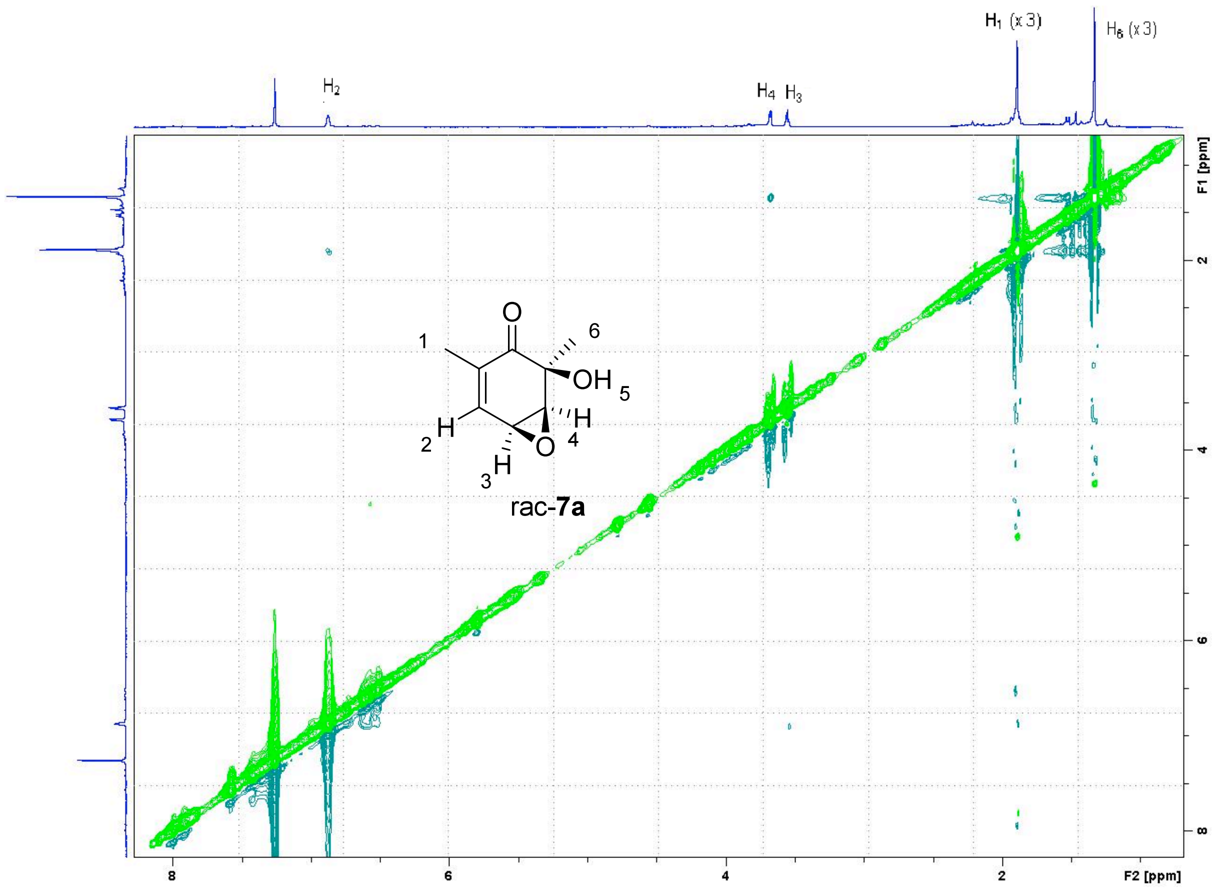
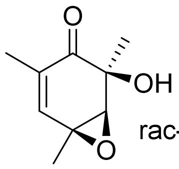
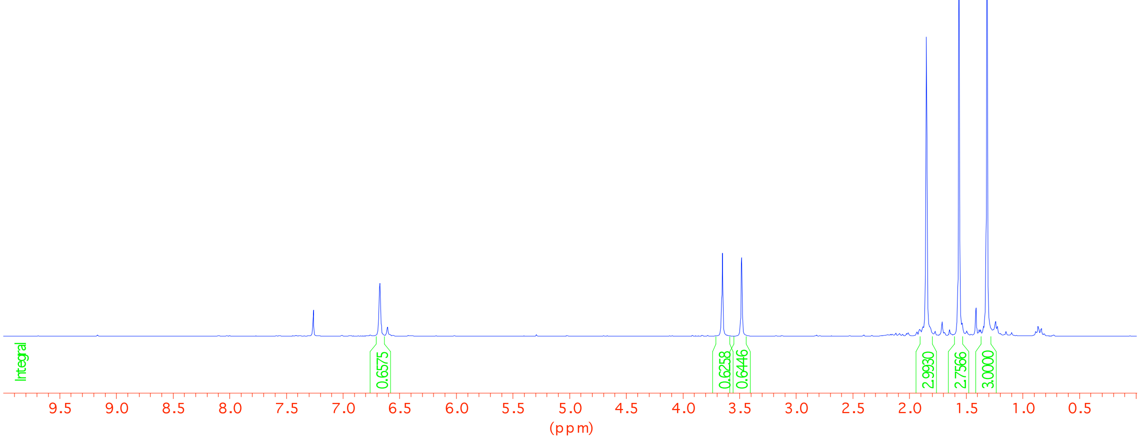
77.0000
76.5771
74.9659
55.9669
47.5756
24.6105
15.7745
OH
rac-7a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)


H2
H4 H3
H1 (x 3)
H6 (x 3)
OH 5
rac-7a
F1 [ppm]
F2 [ppm]

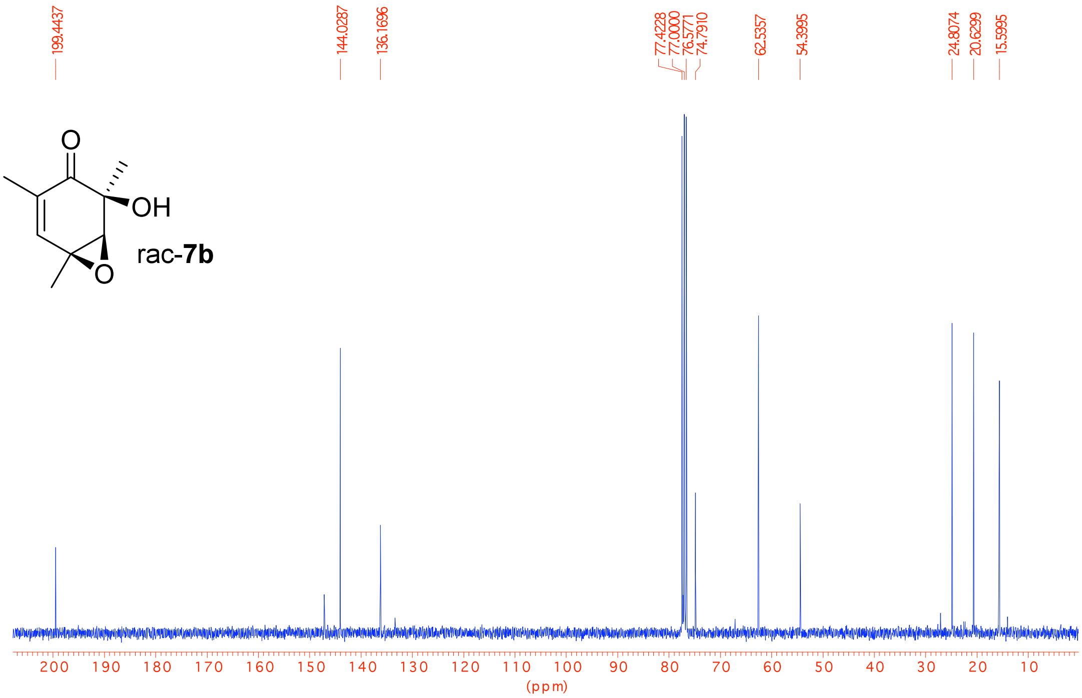


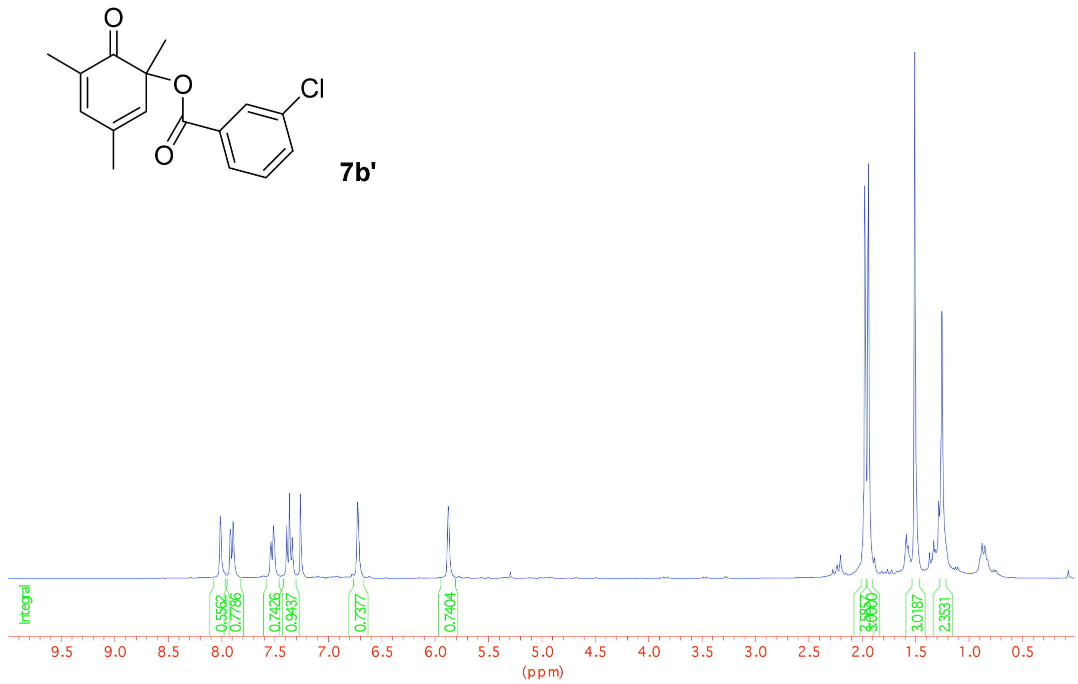
rac-**7b**



Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14630	2178.94	7.2600	25008026	6.0
2	15563	2002.75	6.6729	50937832	12.1
3	20367	1095.53	3.6502	79946176	19.1
4	20636	1044.73	3.4809	75495792	18.0
5	23228	555.24	1.8500	287644480	68.6
6	23235	553.92	1.8456	235992592	56.3
7	23686	468.75	1.5618	397811936	94.8
8	24078	394.72	1.3152	419455808	100.0

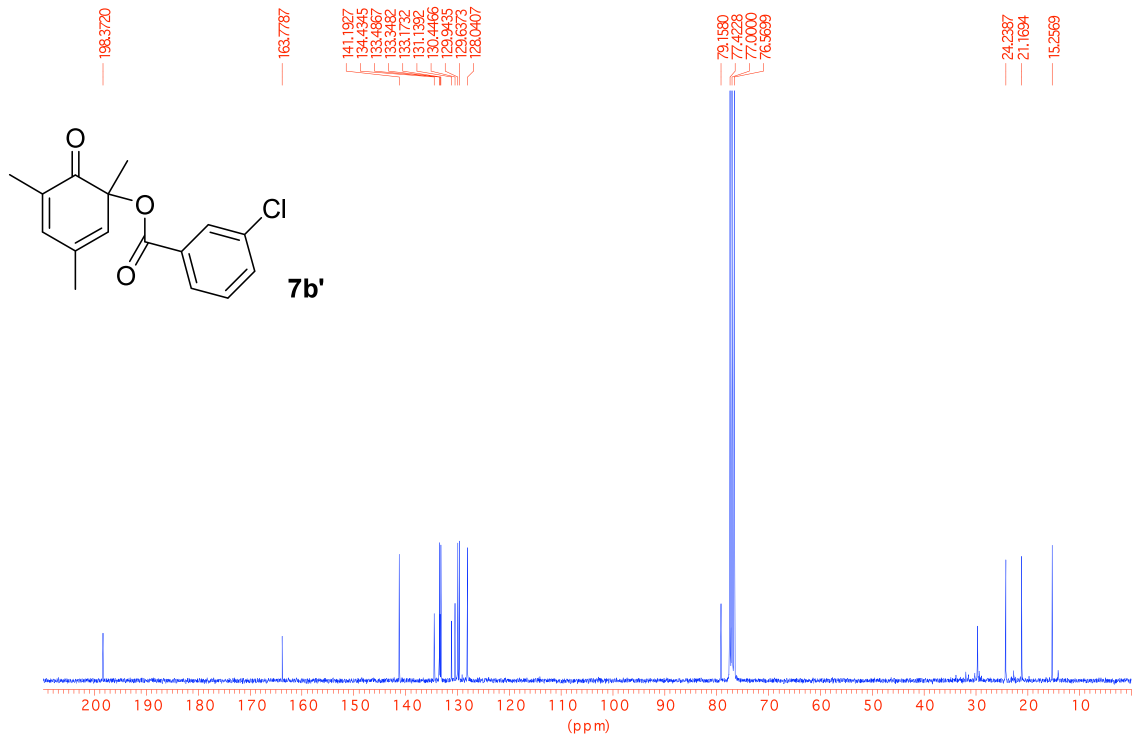


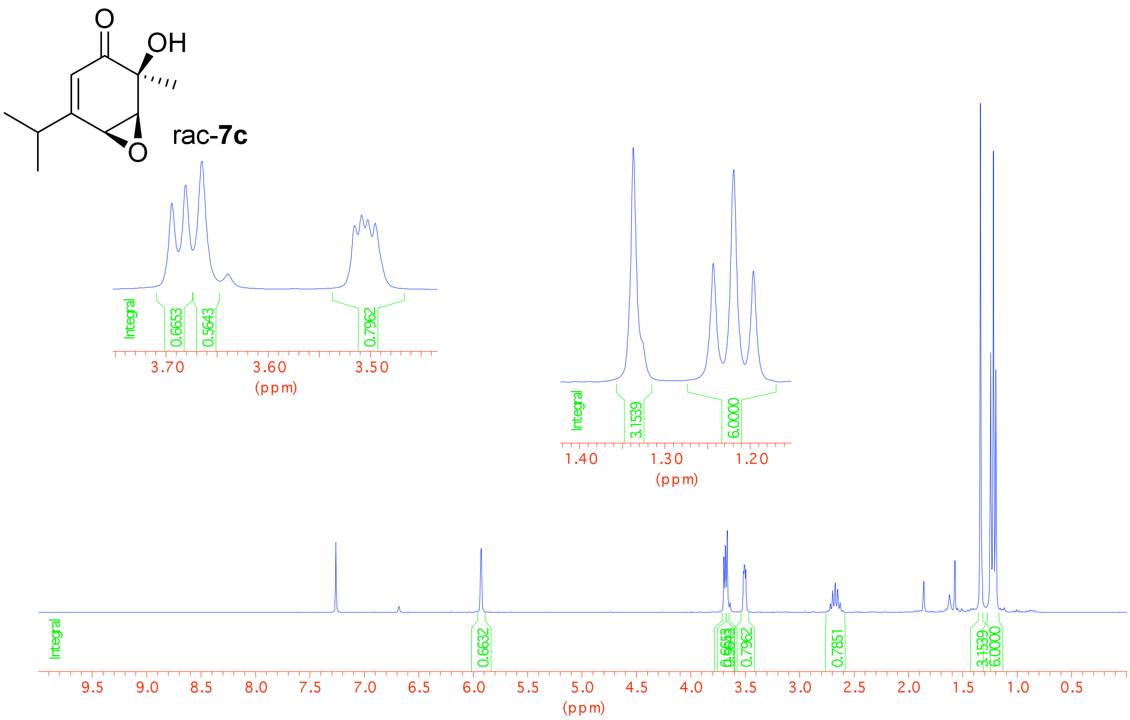


Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13436	2403.86	8.0094	46560792	11.7
2	13583	2376.10	7.9169	36920840	9.3
3	13624	2368.36	7.8911	43122912	10.8
4	14187	2262.04	7.5369	27357340	6.9
5	14191	2261.28	7.5343	26478510	6.7
6	14229	2254.10	7.5104	39915984	10.0

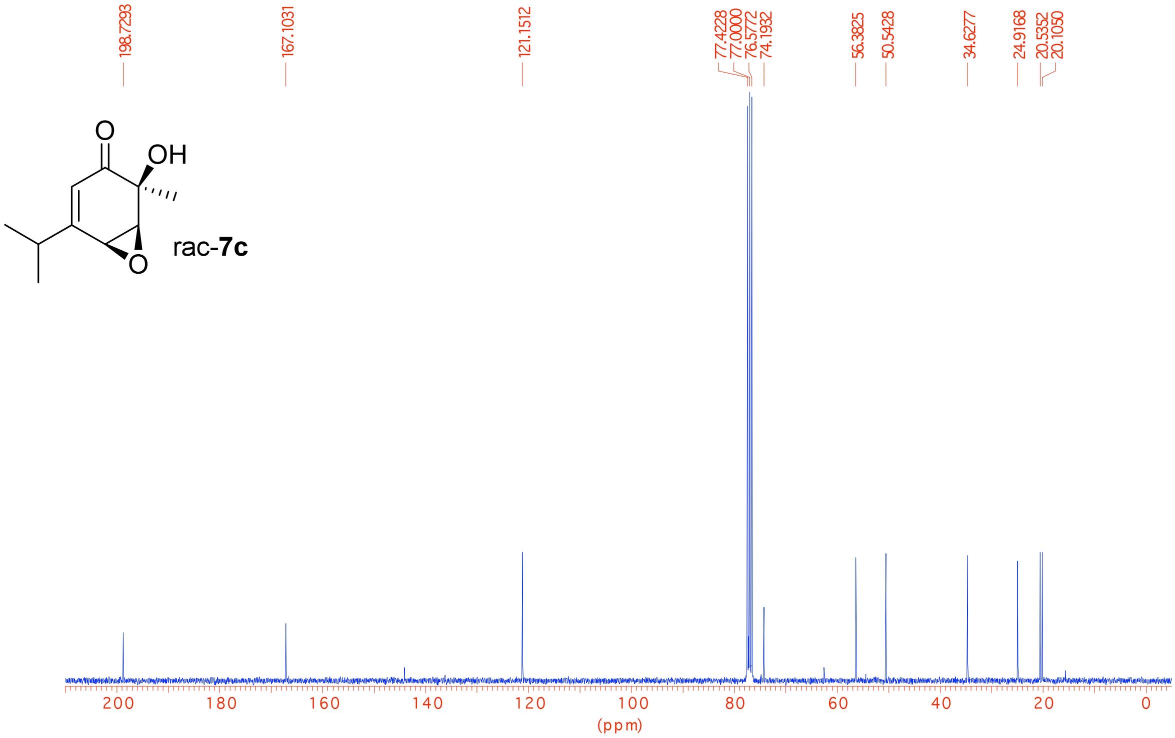
7	14423	2217.47	7.3884	39684536	10.0
8	14464	2209.73	7.3626	64277056	16.2
9	14506	2201.79	7.3361	30929100	7.8
10	14627	2178.94	7.2600	63591680	16.0
11	15480	2017.86	6.7233	57556296	14.5
12	16828	1763.29	5.8751	54594732	13.7
13	23027	592.63	1.9746	296534976	74.6
14	23080	582.63	1.9412	313556096	78.9
15	23770	452.32	1.5071	397587648	100.0



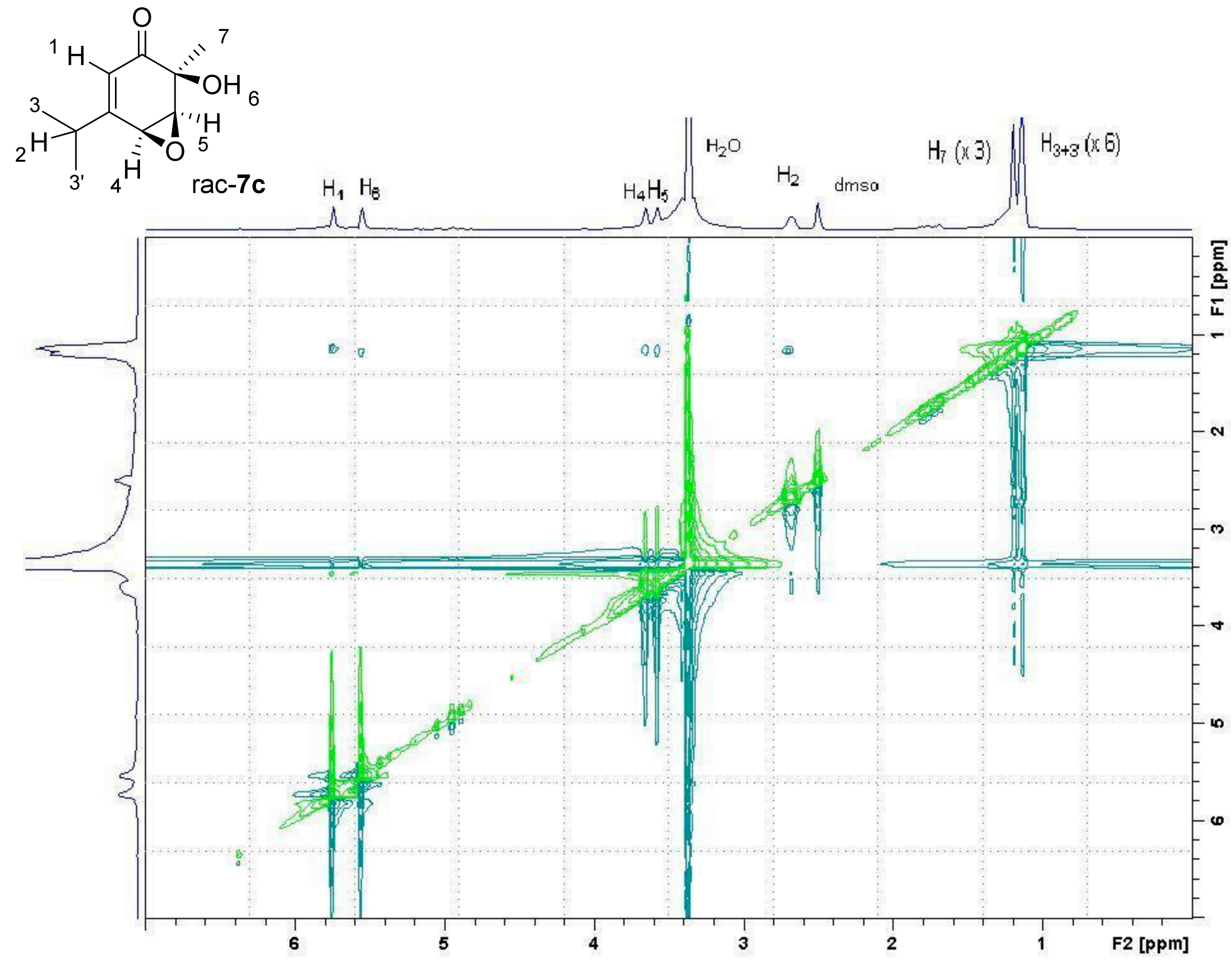


Peak Picking results:

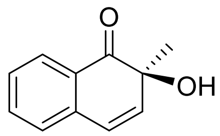
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14628	2178.94	7.2600	78099496	13.8
2	16749	1778.40	5.9254	70979392	12.6
3	20295	1108.75	3.6942	61852948	10.9
4	20316	1104.79	3.6810	74373896	13.2
5	20342	1099.88	3.6647	91207256	16.1
6	20580	1054.93	3.5149	45648808	8.1
7	20590	1053.04	3.5086	53031968	9.4
8	20600	1051.15	3.5023	49848580	8.8
9	20612	1048.89	3.4948	47169992	8.3
10	21848	815.47	2.7171	9801386	1.7
11	21884	808.67	2.6944	24212942	4.3
12	21920	801.88	2.6718	32746908	5.8
13	21955	795.27	2.6497	25617146	4.5
14	21991	788.47	2.6271	10952352	1.9
15	24042	401.14	1.3366	565469056	100.0
16	24191	373.01	1.2428	288122624	51.0
17	24229	365.83	1.2189	512456128	90.6
18	24266	358.84	1.1956	269533952	47.7



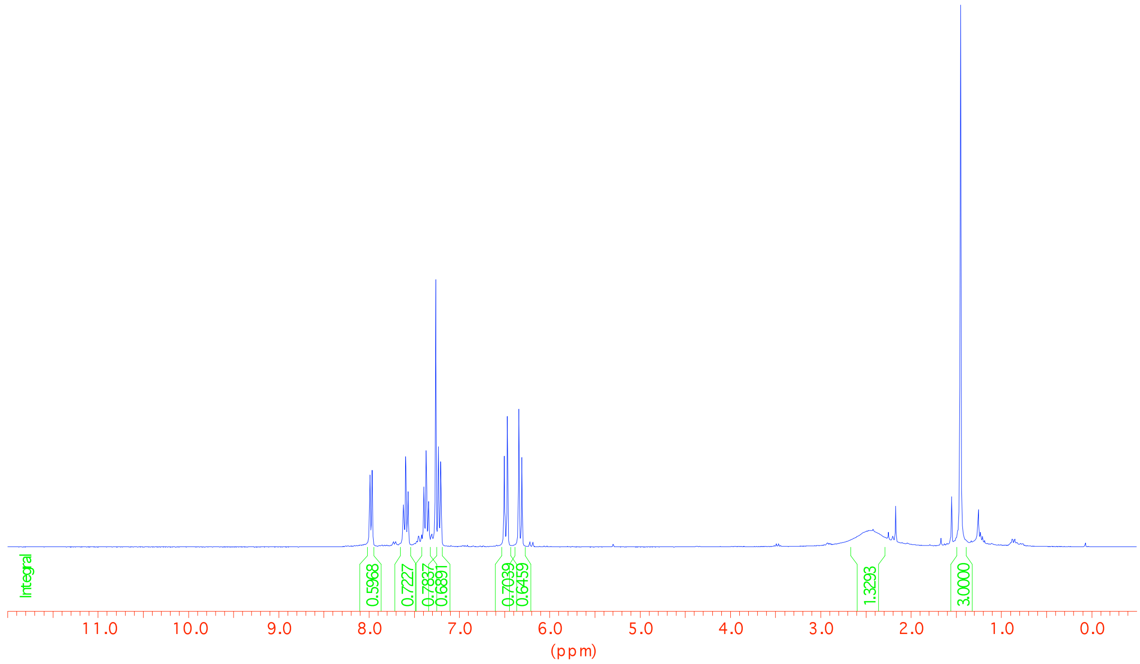
198.7293
167.1031
121.1512
77.4228
77.0000
76.5772
74.1932
56.3825
50.5428
34.6277
24.9168
20.5352
20.1050
rac-7c
(ppm)



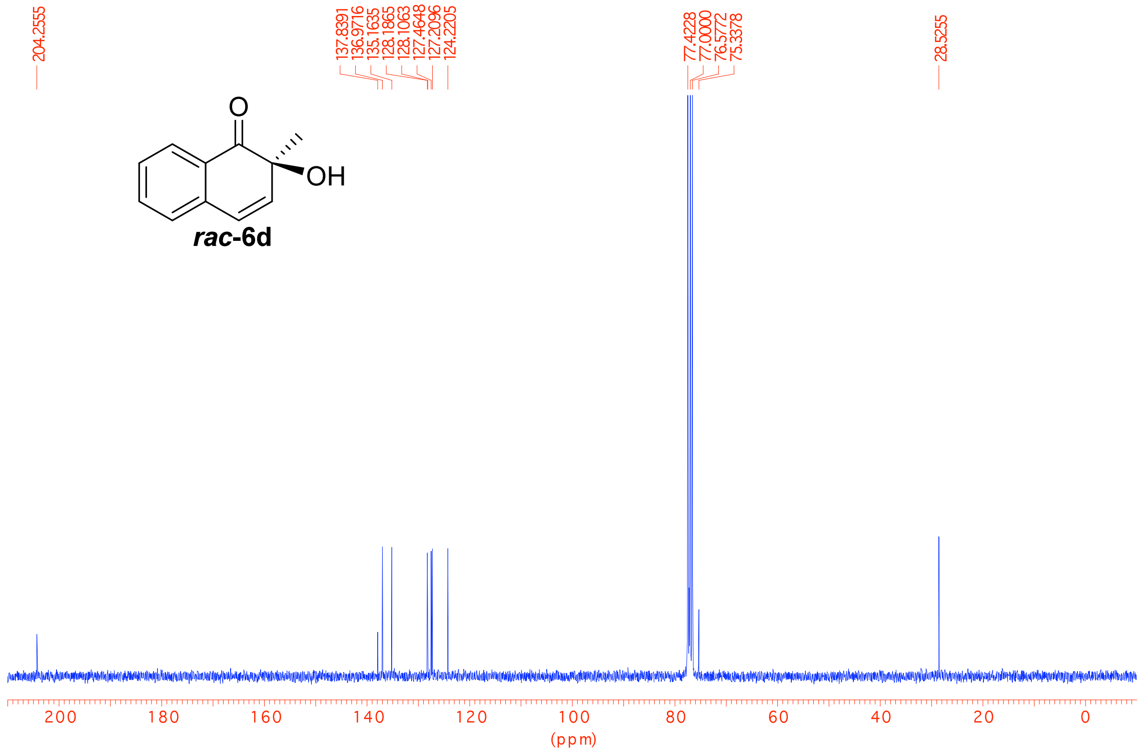
rac-7c
H1
H6
H4H5
H2O
H2
dmso
H7 (x 3)
H3+3' (x 6)
F1 [ppm]
F2 [ppm]



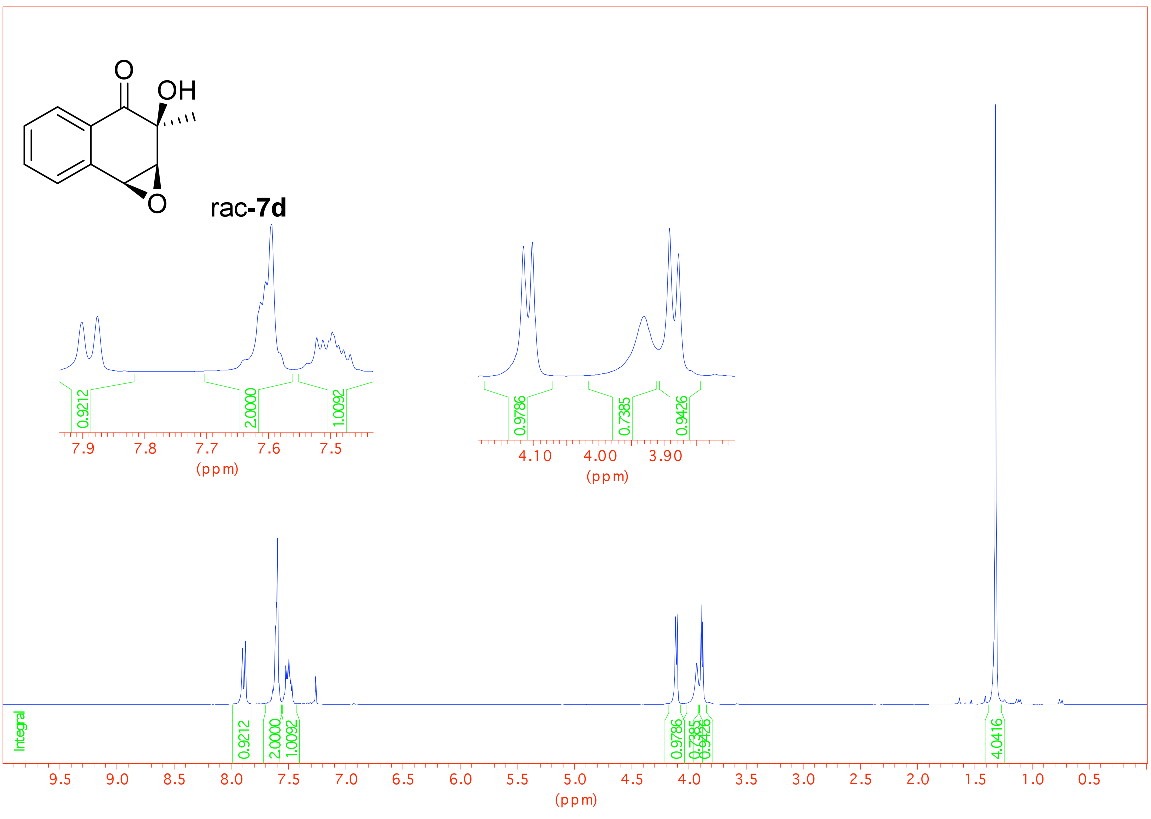
rac-**6d**



Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13470	2397.82	7.9893	39390104	6.6
2	13509	2390.45	7.9647	41967992	7.1
3	14060	2286.40	7.6180	23092304	3.9
4	14066	2285.26	7.6142	21076078	3.6
5	14100	2278.84	7.5929	49360248	8.3
6	14106	2277.71	7.5891	43193756	7.3
7	14140	2271.29	7.5677	30356216	5.1
8	14146	2270.16	7.5639	25772684	4.3
9	14421	2218.22	7.3909	32738220	5.5
10	14461	2210.67	7.3657	52623060	8.9
11	14501	2203.12	7.3405	24958458	4.2
12	14629	2178.94	7.2600	146402112	24.7
13	14676	2170.07	7.2304	54877632	9.3
14	14717	2162.33	7.2046	46612408	7.9
15	15838	1950.63	6.4993	49607400	8.4
16	15890	1940.81	6.4666	71390264	12.0
17	16094	1902.28	6.3382	75361912	12.7
18	16146	1892.46	6.3055	48895144	8.2
19	22252	739.37	2.4635	9013057	1.5
20	23860	435.70	1.4517	593252352	100.0

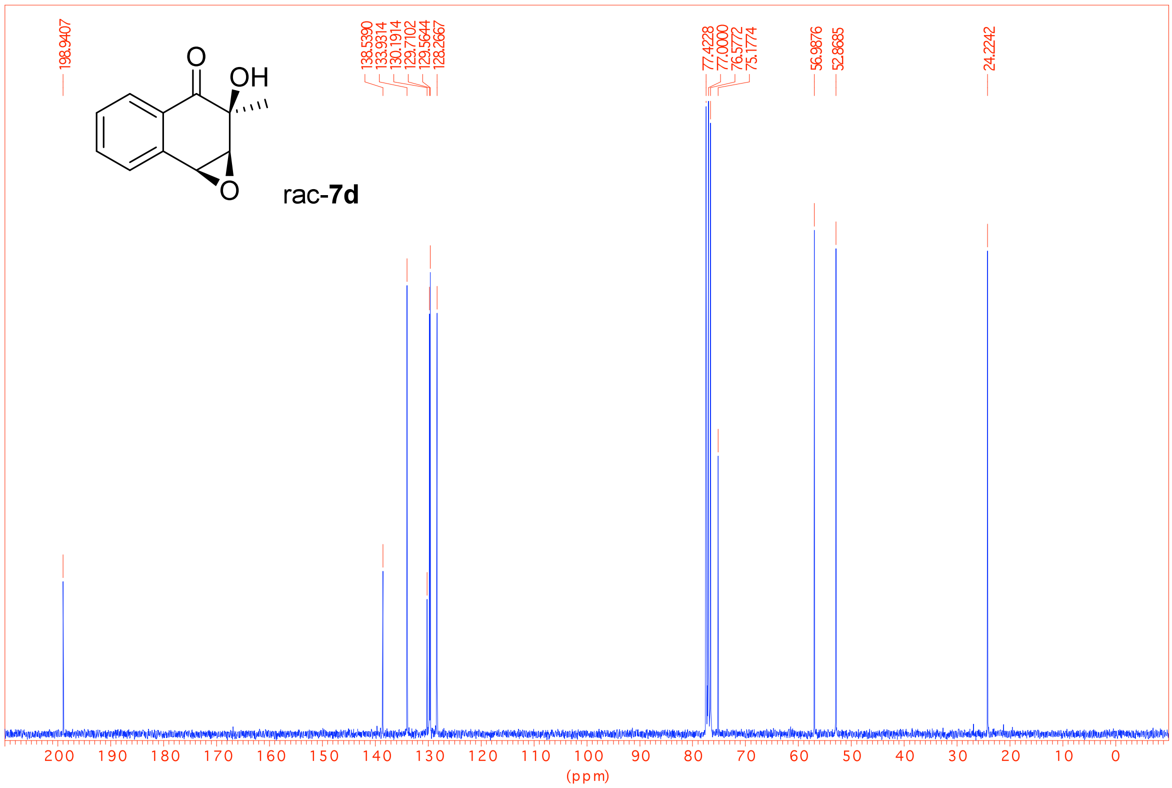


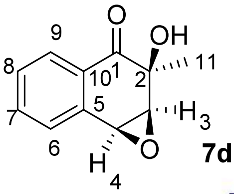
204.2555
137.8391
136.9716
135.1635
128.1865
128.1063
127.4648
127.2096
124.2205
77.4228
77.0000
76.5772
75.3378
28.5255
O
OH
rac-6d
200
180
160
140
120
100
(ppm)
80
60
40
20
0



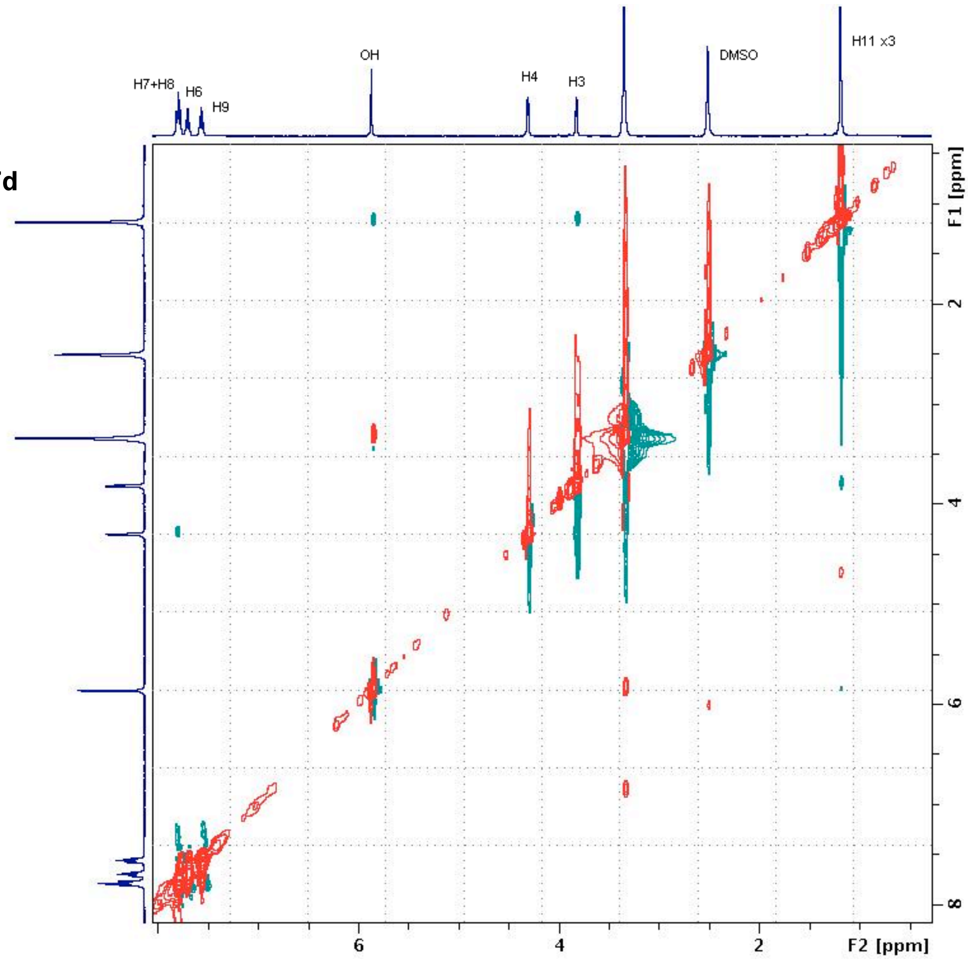
O
OH
O
rac-7d
0.9212
2.0000
1.0092
7.9
7.8
7.7
7.6
7.5
(ppm)
0.9786
0.7385
0.9426
4.10
4.00
3.90
(ppm)
Integral
4.0416
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13610	2371.38	7.9012	23433086	7.7
2	13650	2363.82	7.8760	26273248	8.6
3	14069	2284.70	7.6124	32815512	10.7
4	14082	2282.24	7.6042	42403588	13.9
5	14097	2279.41	7.5947	69337920	22.7
6	14117	2275.63	7.5822	8981979	2.9
7	14213	2257.50	7.5218	16232724	5.3
8	14228	2254.67	7.5123	15121927	5.0
9	14244	2251.65	7.5022	14677050	4.8
10	14253	2249.95	7.4966	18873904	6.2
11	14269	2246.93	7.4865	12647364	4.1
12	14282	2244.47	7.4783	10459460	3.4
13	14299	2241.26	7.4676	8261901	2.7
14	14629	2178.94	7.2600	11674538	3.8
15	19627	1235.09	4.1152	36631532	12.0
16	19649	1230.93	4.1013	37599344	12.3
17	19921	1179.57	3.9302	17115872	5.6
18	19983	1167.86	3.8912	41584304	13.6
19	20005	1163.71	3.8773	34445800	11.3
20	24073	395.48	1.3177	305372160	100.0




OH
9
8
10
1
2
11
5
H
3
7
6
O
H
4

7d


H7+H8
H6
H9
OH
H4
H3
DMSO
H11 x3
F1 [ppm]
F2 [ppm]
2
4
6
8